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(54) Title: IMPROVED LUBRICATING COMPOSITIONS AND ADDITIVES USEFUL THEREIN

(57) Abstract

This invention relates to compositions comprising a major amount of an oil of lubricating viscosity, (A) a metal salt selected from the group consisting of sulfonates, phenates, carboxylates and mixtures thereof, (B) an aliphatic carboxylic acid or anhydride, or carboxylic acid containing derivative thereof, wherein the aliphatic group contains at least about 20 carbon atoms and optionally (C) a metal salt of (C) (I) at least one organic phosphorus acid or a mixture of (C) (I) at least one organic phosphorus acid and (C) (II) at least one carboxylic acid. Also disclosed are lubricants and functional fluids containing these additives, methods for improving the wet filterability of lubricants and functional fluids, and means for retaining zinc when zinc-containing compositions are exposed to water.

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TITLE: IMPROVED LUBRICATING COMPOSITIONS AND ADDITIVES USEFUL THEREIN

FIELD OF THE INVENTION

This invention relates to compositions useful as additives for lubricants and functional fluids, and to additive concentrates, lubricants and functional fluids containing said additives. More particularly, this invention relates to compositions comprising a major amount of an oil of lubricating viscosity, (A) a metal salt selected from the group consisting of sulfonates, phenates, carboxylates and mixtures thereof, (B) an aliphatic carboxylic acid or anhydride, or carboxylic acid containing derivative thereof, wherein the aliphatic group contains at least about 20 carbon atoms and optionally (C) a metal salt of (C)(I) at least one organic phosphorus acid or a mixture of (C)(I) at least one organic phosphorus acid and (C)(II) at least one carboxylic acid. Also disclosed are lubricants and functional fluids containing these additives and methods for improving the wet filterability of lubricants and functional fluids. This invention also relates to the retention of zinc when compositions containing zinc-containing additives are exposed to water.

BACKGROUND OF THE INVENTION

Depending upon their intended use, lubricants are required to meet a variety of performance requirements. It is known in the art to add various chemical additives

to a lubricating oil basestock in order to provide or reinforce needed properties.

For very mild applications, the lubricant may contain nothing more than the lubricating base stock, although even in this case, additives such as oxidation and corrosion inhibitors and antifoam agents are often included.

More often, especially when lubricating machinery such as engines, gears, transmissions, hydraulic systems and the like, it is necessary that the lubricant provides some degree of antiwear and extreme pressure performance.

Chemical additives to provide extreme pressure and antiwear performance are known. These include, but are not limited to, phosphorus-containing additives, sulfur-containing additives and others. Phosphorus additives include metal-free and metal-containing derivatives of phosphorus acids.

Adams et al, U.S. 4,938,884, describes phosphorus-containing coupled amides as lubricating oil additives.

Hoke (U.S. Patents 4,032,461; 4,208,357; and 4,282,171, refers to various phosphorus and sulfur-containing amides and thioamides.

Metal salts of phosphorodithioic acids are known lubricant additives. See, for example, Le Suer et al, U.S. 3,390,082 and Chamberlin, U.S. 4,326,974.

Metals salts of mixtures of carboxylic and phosphorus acids are also known, as are post-treated metal salts of phosphorus acids. See, for example, Clason et al, U.S. 4,308,154, Schroeck, U.S. 4,289,635, Schroeck, U.S. 4,507,215 and Schroeck, U.S. 4,263,150.

Metals salts of organic acids, and particularly overbased metal salts of organic acids are also well-known lubricating oil additives.

Grover, in U.S. 4,466,894, describes lubricants having, inter alia, improved hydrolytic stability.

For many applications, lubricating oils described in the aforementioned patents provide exemplary performance. However, in several applications, it has been found to be desirable, and sometimes necessary, that the lubricant possess even further enhanced performance characteristics.

Many lubricating oil compositions such as functional fluids, and especially hydraulic fluids, are used in equipment designed to very close tolerances. For example, a hydraulic fluid which is employed as the lubricant and power transmitting fluid in hydraulic pumps must provide extreme pressure, antiwear and oxidation performance. Because of the close operating tolerances, it is usually necessary that hydraulic fluids be kept meticulously clean. To accomplish this end, very fine filters are employed to remove solid contaminants from the circulating hydraulic fluid. The filter must remove abrasive contaminants, but still must allow free fluid flow through the system.

It has been recently observed that lubricating oil compositions, including hydraulic fluids, containing metal salts of organic acids, and particularly those containing overbased metal salts, when exposed to moisture, may clog filters. Such moisture may arise from, for example, environmental contamination or condensation of atmospheric moisture. When the filters become clogged, fluid flow is reduced, or in extreme cases, essentially stops. Filterability of moisture (water) containing lubricating compositions is referred to herein as wet filterability.

The nature of the moisture-contaminated lubricating oil is not understood, that is, it is not known with certainty whether, for example, the moisture (water) is simply dispersed within the oil composition, whether a chemical reaction has taken place or if the moisture is incorporated in some other fashion. What is known is that when the oil composition is contaminated with

moisture, filterability, especially filterability through fine filters, is impaired.

In general, moisture contamination contributing to filterability difficulties is present in the oil composition in amounts ranging up to about 1% by weight of the oil composition, although more than 1% by weight of water may be present as a contaminant and may contribute to filterability difficulties.

It has also been observed with zinc-containing lubricating oil compositions that, when the oil composition is exposed to water, loss of zinc from the lubricating oil composition may take place. In some cases as much as 50% or even more of the zinc originally present may be lost. Since zinc compounds are frequently used to provide enhanced antiwear and/or antioxidancy, loss of zinc may result in reduced performance.

Accordingly, it would be beneficial to provide a lubricant or functional fluid that does not tend to generate materials that clog filters when the fluid is exposed to moisture. Likewise, it would be beneficial if a zinc-containing lubricating oil composition resisted loss of zinc when the oil is exposed to water.

SUMMARY OF THE INVENTION

The present invention provides compositions useful as additives for lubricants and additive concentrates and lubricants containing these additives. Lubricants and functional fluids containing these additives have a reduced tendency to clog filters when the lubricants are exposed to moisture and resist depletion of zinc when exposed to water.

The present invention provides a composition comprising a major amount of an oil of lubricating viscosity, and minor amounts of (A) a metal salt selected from the group consisting of sulfonates, phenates, carboxylates and mixtures thereof, (B) an aliphatic carboxylic acid or anhydride, or carboxylic-acid group containing

derivative thereof, wherein the aliphatic group contains at least about 20 carbon atoms and optionally (C) a metal salt of (C)(I) at least one organic phosphorus acid or mixture of (C)(I) at least one organic phosphorus acid and (C)(II) at least one carboxylic acid. Component (B) is present in an effective amount to improve wet filterability of the composition. In another embodiment, the composition may comprise a phosphite. These compositions are useful as lubricating compositions, and functional fluids, such as hydraulic fluids.

Further, the present invention provides a method for improving the wet filterability of lubricants and functional fluid compositions. Also provided is a method for imparting to lubricating oil compositions the ability to resist depletion of zinc when the compositions are exposed to water.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The term "hydrocarbon based group" is used throughout this specification and in the appended claims to denote a group having a carbon atom directly attached to the remainder of the molecule and having a predominantly hydrocarbon character within the context of this invention. Thus, the term "hydrocarbon based group" includes hydrocarbon, as well as substantially hydrocarbon, groups. Substantially hydrocarbon describes groups may contain non-hydrocarbon substituents, or non-carbon atoms in a ring or chain, which do not alter the predominantly hydrocarbon nature of the group.

Hydrocarbon based groups can contain up to three, preferably up to one, non-hydrocarbon substituent, or non-carbon heteroatom in a ring or chain, for every ten carbon atoms, provided this non-hydrocarbon substituent or non-carbon heteroatom does not significantly alter the predominantly hydrocarbon character of the group. Preferably, hydrocarbon-based groups are purely hydrocarbon, that is, they are substantially free of

non-hydrocarbon substituents or heteroatoms. Those skilled in the art will be aware of such heteroatoms, such as oxygen, sulfur and nitrogen, or substituents, which include, for example, hydroxyl, halo (especially chloro and fluoro), alkoxyl, alkyl mercapto, alkyl sulfoxy, etc.

Examples of hydrocarbon based groups include, but are not necessarily limited to, the following:

(1) hydrocarbon groups, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) groups, aromatic-, aliphatic- and alicyclic-substituted aromatic groups and the like as well as cyclic groups wherein the ring is completed through another portion of the molecule (that is, for example, any two indicated substituents may together form an alicyclic radical);

(2) substituted hydrocarbon groups, that is, those groups containing non-hydrocarbon groups or atoms which, in the context of this invention, do not alter the predominantly hydrocarbon character of the group; those skilled in the art will be aware of such groups (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.);

(3) hetero groups, that is, groups which will, while having a predominantly hydrocarbon character within the context of this invention, contain atoms other than carbon present in a ring or chain otherwise composed of carbon atoms. Suitable heteroatoms will be apparent to those of ordinary skill in the art and include, for example, sulfur, oxygen, nitrogen and such substituents as, e.g., pyridyl, furyl, thienyl, imidazolyl, etc. In general, no more than about 2, preferably no more than one, non-hydrocarbon substituent or non-carbon atom in a ring moiety, will be present for every ten carbon atoms in the hydrocarbyl group. More preferred, however, the hydrocarbyl groups are purely hydrocarbon and contain

substantially no such non-hydrocarbon groups or substituents.

(A) The Metal Sulfonate, Phenate or Carboxylate

Component (A) is a metal salt selected from the group consisting of sulfonates, phenates or carboxylates. These salts may be normal salts or they may be overbased salts. Overbased salts are preferred.

The metals may be alkali or alkaline earth metals, copper or zinc. In a preferred embodiment the metals are alkali or alkaline earth metals, more preferably, sodium, potassium, calcium or magnesium.

The Normal Metal Salt

Component (A) may be a normal metal salt, that is, a salt wherein the metal content is substantially that which is present according to the stoichiometry of the metal and the particular organic compound reacted with the metal. These salts are sometimes referred to as "neutral" salts despite the fact that, depending upon the nature of the anion and cation, the salt may display basic properties, i.e., may display basic character as opposed to neutral or acidic character, especially in aqueous media. For the purposes of this invention, metal salts of sulfonic acids, phenols and carboxylic acids are preferred. Preferred metals are alkali or alkaline earth metals, copper or zinc. Normal metal salts are readily prepared by the reaction of an acid with a metal compound such as a hydroxide or carbonate, double displacement reactions, such as the reaction of a sodium salt with calcium chloride, etc. The skilled worker is aware of numerous means for preparing normal metal salts, and further elaboration here is unnecessary.

The Overbased Metal Salt

The terms "overbased," "superbased," and "hyperbased," are terms of art which are generic to well-known classes of metal-containing materials which have generally been employed as detergents and/or dispersants in lubricating oil compositions. Overbased

materials are characterized by a metal content in excess of that which would be present according to the stoichiometry of the metal and the particular organic compound reacted with the metal, e.g., a carboxylic or sulfonic acid or phenol. Thus, if a monocarboxylic acid,

$$R - \overset{\overset{\displaystyle O}{\|}}{C} - OH$$

is neutralized with a basic metal compound, e.g., calcium hydroxide, the "normal" metal salt produced will contain one equivalent of calcium for each equivalent of acid, i.e.,

$$R - \overset{\overset{\displaystyle O}{\|}}{C} - O - Ca - O - \overset{\overset{\displaystyle O}{\|}}{C} - R \quad .$$

However, as is well known in the art, various processes are are available which result in an inert organic liquid solution of a product containing more than the stoichiometric amount of metal. The solutions of these products are referred to herein as overbased materials. Following these procedures, the carboxylic acid or an alkali or alkaline earth metal salt thereof can be reacted with a metal base and the product will contain an amount of metal in excess of that necessary to neutralize the acid, for example, 4.5 times as much metal as present in the normal salt or a metal excess of 3.5 equivalents.

The actual stoichiometric excess of metal can vary considerably, for example, from about 0.1 equivalent to about 50 or more equivalents depending on the reactions, the process conditions, and the like. The overbased materials useful in accordance with the present invention contain from about 1.1 to about 40 or more equivalents of metal, more preferably from about 1.5 to about 30 and most preferably from about 2 to about 25 equivalents of metal for each equivalent of material which is overbased.

In the present specification and claims the term "overbased" is used to designate materials containing a stoichiometric excess of metal and is, therefore, inclusive of those materials which have been referred to in the art as overbased, superbased, hyperbased, etc., as discussed supra, and hereinbelow.

It is recognized herein that in many chemical reactions, slightly more or slightly less of a component may be incorporated into the resulting product. In the present case, it is recognized that very small amounts of excess metal may be incorporated into what is otherwise a substantially neutral product. For the purposes of this invention, such products are not considered "overbased".

The terminology "metal ratio" is used in the prior art and herein to designate the ratio of the total chemical equivalents of the metal in the overbased material (e.g., a metal sulfonate or carboxylate) to the chemical equivalents of the metal in the product which would be expected to result in the reaction between the organic material to be overbased (e.g., sulfonic or carboxylic acid) and the metal-containing reactant (e.g., calcium hydroxide, barium oxide, etc.) according to the known chemical reactivity and stoichiometry of the two reactants.

The equivalent weight of the acidic organic compound is its molecular weight divided by the number of acidic groups (i.e., sulfonic acid, carboxy or acidic hydroxy groups) present per molecule. In many cases the acidic organic compound contains a diluent such as oil or unreacted alkylate. Often the acidic organic compound is not a pure single species. In these and in other situations as appropriate, the equivalent weight of the acidic organic compound can be determined by a suitable analytical technique such as acid number (e.g. ASTM procedures D-664 and/or D-974). Thus, in the normal calcium carboxylate discussed above, the metal ratio is one, and in the overbased carboxylate, the metal ratio

may be 4.5. Obviously, if there is present in the material to be overbased more than one compound capable of reacting with the metal, the "metal ratio" of the product will depend upon whether the number of equivalents of metal in the overbased product is compared to the number of equivalents expected to be present for a given single component or a combination of all such components.

The metal ratio may be expressed in terms of percentages. For a normal metal salt, the percentage is 100%; for overbased materials, the percentage is greater than 100. For the overbased calcium carboxylate example above, the percentage is 450.

Generally, overbased materials are prepared by treating a reaction mixture comprising the organic material to be overbased, a reaction medium consisting essentially of at least one inert, organic solvent for said organic material, a stoichiometric excess of a metal base, and a promoter with an acidic material. Methods for preparing the overbased materials for use in the present invention, as well as an extremely diverse group of overbased materials, are well known in the art and are disclosed for example in the following U.S. Patent Nos. 2,616,904; 2,616,905; 2,616,906, 2,616,911; 2,616,924; 2,616,925; 2,617,049; 2,695,910; 2,723,234; 2,723,235; 2,723,236; 2,760,970; 2,767,164; 2,767,209; 2,777,874; 2,798,852; 2,839,470; 2,856,359; 2,859,360; 2,856,361; 2,861,951; 2,883,340; 2,915,517; 2,959,551; 2,968,642; 2,971,014; 2,989,463; 3,001,981; 3,027,325; 3,070,581; 3,108,960; 3,147,232; 3,133,019; 3,146,201; 3,152,991; 3,155,616; 3,170,880; 3,170,881; 3,172,855; 3,194,823; 3,223,630; 3,232,883; 3,242,079; 3,242,080; 3,250,710; 3,256,186; 3,274,135; 3,492,231; 4,230,586 and 4,466,894. These patents disclose processes, materials which can be overbased, suitable metal bases, promoters, and acidic materials, as well as a variety of specific overbased

products useful in this invention and are, accordingly, incorporated herein by reference.

An important characteristic of the organic materials which are overbased is their solubility in the particular reaction medium utilized in the overbasing process. As the reaction medium used frequently comprises petroleum fractions, particularly mineral oils, these organic materials have generally been oil-soluble. However, if another reaction medium is employed (e.g., aromatic hydrocarbons, aliphatic hydrocarbons, kerosene, etc.) it is not essential that the organic material be soluble in mineral oil as long as it is soluble in the given reaction medium. Obviously, many organic materials which are soluble in mineral oils will be soluble in many of the other indicated suitable reaction media.

Materials which can be overbased are generally oil-soluble organic acids including sulfonic acids, phosphorus acids, thiophosphorus acids, sulfur acids, alkylphenols, coupled alkylphenols, carboxylic acids, thiocarboxylic acids, and the like, as well as the corresponding alkali and alkaline earth metal salts thereof. Representative examples of each of these classes of organic acids, as well as other organic acids, e.g., nitrogen acids, arsenic acids, etc., are disclosed along with methods of preparing overbased products therefrom in the above-cited patents and are, accordingly, incorporated herein by reference. U.S. Patent No. 2,777,874 identifies organic acids suitable for preparing overbased materials. Similarly, U.S. Patent Nos. 2,616,904; 2,695,910; 2,767,164; 2,767,209; 3,147,232; 3,274,135; etc., disclose a variety of organic acids suitable for preparing overbased materials as well as representative examples of overbased products prepared from such acids. Overbased acids wherein the acid is a phosphorus acid, a thiophosphorus acid, phosphorus acid-sulfur acid combination, and sulfur acid prepared from polyolefins are disclosed in U.S. Patent Nos.

2,883,340; 2,915,517; 3,001,981; 3,108,960 and 3,232,883. Overbased phenates are disclosed in U.S. Patent No. 2,959,551, while overbased ketones are found in U.S. Patent No. 2,798,852. A variety of overbased materials derived from oil-soluble metal-free, non-tautomeric neutral and basic organic polar compounds such as ester, amines, amides, alcohols, ethers, sulfides, sulfoxides, and the like are disclosed in U.S. Patent Nos. 2,968,642; 2,971,014 and 2,989,463. Another class of materials which can be overbased are the oil-soluble, nitro-substituted aliphatic hydrocarbons, particularly nitro-substituted polyolefins such as polyethylene, polypropylene, polyisobutylene, etc. Materials of this type are illustrated in U.S. Patent No. 2,959,551. Likewise, mixtures of alkylated phenols and the oil-soluble reaction product of alkylene polyamines such as propylene diamine or N-alkylated propylene diamine with formaldehyde or formaldehyde producing compound (e.g., paraformaldehyde) can be overbased. The process and products obtained thereby are disclosed in U.S. 3,372,118. Other compounds suitable for overbasing are disclosed in the above-cited patents or are otherwise well-known in the art. For the purposes of this invention, overbased sulfonic acids, phenols and carboxylic acids are preferred.

The metal compounds used in preparing the overbased materials are normally the basic salts, oxides and hydroxides of alkali and alkaline earth metals, although corresponding metal compounds such as lead, zinc, manganese, copper, etc., can be used in the preparation of overbased materials. Mixtures of different metal compounds can be used to prepare mixed metal overbased products. The anionic portion of the metal compound can be hydroxyl, oxide, carbonate, hydrogen carbonate, acetate, hydrogen sulfite, halide, amide, borate, etc., as disclosed in the above-cited patents. For purposes of this invention the preferred overbased materials are

prepared from alkali and alkaline earth metal oxides, hydroxides, and alcoholates such as the alkaline earth metal lower alkoxides. The more preferred metals are calcium, magnesium, sodium, lithium, and/or barium. The most preferred alkali metal is sodium, and calcium is the most preferred alkaline earth metal. As mentioned hereinabove, mixed metal overbased products are also useful.

The promoters, that is, the materials which permit the incorporation of the excess metal into the overbased material, are also quite diverse and well known in the art as evidenced by the cited patents. A particularly comprehensive discussion of suitable promoters is found in U.S. Patent Nos. 2,777,874; 2,695,910 and 2,616,904. These include the alcoholic and phenolic promoters which are preferred. The alcoholic promoters include the alkanols of one to about eighteen carbon atoms, preferably one to about twelve carbon atoms, and more preferably one to about five carbon atoms, such as methanol, ethanol, n-butanol, amyl alcohol, octanol, isopropanol, isobutanol, and mixtures of these and the like. Polyols are also useful promoters. A particularly preferred polyol is ethylene glycol. Phenolic promoters include a variety of hydroxy- substituted benzenes and naphthalenes. A particularly useful class of phenols are the alkylated phenols of the type listed in U.S. Patent No. 2,777,874, e.g., heptylphenols, octylphenols, and nonylphenols. Mixtures of various promoters are sometimes used.

Suitable acidic materials are also disclosed in the above-cited patents, for example, U.S. Patent No. 2,616,904. Included within the known group of useful acidic materials are liquid acids such as formic acid, acetic acid, nitric acid, sulfuric acid, hydrochloric acid, hydrobromic acid, carbamic acid, substituted carbamic acids, etc. Acetic acid is a very useful acidic material, although inorganic acidic materials such as

boric acid, HCl, SO_2, SO_3, CO_2, H_2S, N_2O_3, etc., are ordinarily employed as the acidic materials. The most preferred acidic materials are carbon dioxide and acetic acid, with carbon dioxide being especially preferred.

When the metal reactant used in the overbasing process is an oxide or alkoxide, H_2O can be used as the acidic material. Examples include overbasing with MgO or aluminum isopropoxide.

In preparing overbased materials, the material to be overbased, an inert, non-polar, organic solvent therefor, the metal base, the promoter and the acidic material are brought together and a chemical reaction ensues. The exact nature of the resulting overbased product is not known. However, it can be adequately described for purposes of the present specification as a single phase homogeneous mixture of the solvent and (1) either a metal complex formed from the metal base, the acidic material, and the material being overbased and/or (2) an amorphous metal salt formed from the reaction of the acidic material with the metal base and the material which is said to be overbased. Thus, if mineral oil is used as the reaction medium, carboxylic acid as the material which is overbased, $Ca(OH)_2$ as the metal base, and carbon dioxide as the acidic material, the resulting overbased material can be described for purposes of this invention as an oil solution of either a metal-containing complex of the acidic material, the metal base, and the carboxylic acid or as an oil solution of amorphous calcium carbonate and calcium carboxylate.

The temperature at which the acidic material is contacted with the remainder of the reaction mass depends to a large measure upon the promoting agent used. With a phenolic promoter, the temperature usually ranges from about 80°C to 300°C, and preferably from about 100°C to about 200°C. When an alcohol or mercaptan is used as the promoting agent, the temperature usually will not exceed

the reflux temperature of the reaction mixture and preferably will not exceed about 100°C.

In view of the foregoing, it should be apparent that the overbased materials may retain all or a portion of the promoter. That is, if the promoter is not volatile (e.g., an alkyl phenol) or otherwise readily removable from the overbased material, at least some promoter remains in the overbased product. The presence or absence of the promoter in the overbased material does not represent a critical aspect of the invention. Obviously, it is within the skill of the art to select a volatile promoter such as a lower alkanol, e.g., methanol, ethanol, etc., so that the promoter can be readily removed prior to incorporation within the compositions of the present invention.

One preferred class of overbased materials is the metal-overbased water-insoluble organic acids, preferably those containing at least eight aliphatic carbons, although the acids may contain as few as six aliphatic carbon atoms if the acid molecule includes an aromatic ring such as phenyl, naphthyl, etc. Representative organic acids suitable for preparing these overbased materials are discussed and identified in detail in the above-cited patents. In particular, U.S. Patent Nos. 2,616,904 and 2,777,874 disclose a variety of very suitable organic acids. Overbased carboxylic and sulfonic acids and phenols are particularly suitable.

Suitable carboxylic acids include aliphatic, cycloaliphatic and aromatic mono- and polybasic carboxylic acids free from acetylenic unsaturation, including naphthenic acids, alkyl- or alkenyl-substituted cyclopentanoic acids, alkyl- or alkenyl-substituted cyclohexanoic acids, and alkyl- or alkenyl-substituted aromatic carboxylic acids. The aliphatic acids generally contain from about 8 to about 50, and preferably from about 12 to about 25, carbon atoms. The cycloaliphatic and aliphatic carboxylic acids can be saturated or

unsaturated. Specific examples include 2-ethylhexanoic acid, linolenic acid, propylene tetramer-substituted maleic acid, behenic acid, isostearic acid, pelargonic acid, capric acid, palmitoleic acid, linoleic acid, lauric acid, oleic acid, ricinoleic acid, undecylic acid, dioctylcyclopentanecarboxylic acid, myristic acid, dilauryldecahydronaphthalene-carboxylic acid, stearyl-octahydroindenecarboxylic acid, palmitic acid, alkyl- and alkenylsuccinic acids, acids formed by oxidation of petrolatum or of hydrocarbon waxes, and commercially available mixtures of two or more carboxylic acids, such as tall oil acids, rosin acids, and the like.

Other carboxylic acids include propenyl-substituted glutaric acid, polybutenyl-substituted succinic acids derived from a polybutene (Mn equals about 200-1500, preferably about 300-1500), propenyl-substituted succinic acids derived from polypropylenes (Mn equals 200-1000), acids, acids formed by oxidation of petrolatum or of hydrocarbon waxes, available mixtures of two or more carboxylic acids and mixtures of these acids, their metal salts, and/or their anhydrides.

In one embodiment, the carboxylic acids are aromatic carboxylic acids. A group of useful aromatic carboxylic acids are those of the formula

$$(R_1)_a\text{—}Ar\begin{cases}(\overset{X}{\overset{\|}{C}}\text{-}XH)_b \\ (XH)_c\end{cases}$$

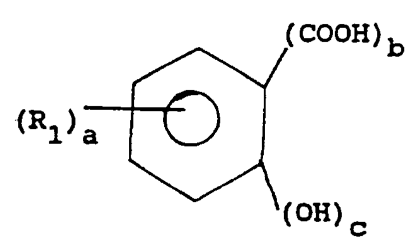
wherein R_1 is an aliphatic hydrocarbon based group preferably derived from polyalkenes, a is a number in the range of 1 to about 4, usually 1 or 2, Ar is an aromatic group, each X is independently sulfur or oxygen, preferably oxygen, b is a number in the range of from 1 to about 4, usually 1 or 2, c is a number in the range of

zero to about 4, usually 1 to 2, with the proviso that the sum of a, b and c does not exceed the number of valences of Ar. Examples of aromatic carboxylic acids include substituted benzoic, phthalic and salicylic acids.

The R_1 group is a hydrocarbon based group that is directly bonded to the aromatic group Ar. Examples of R_1 groups include substituents derived from polymerized olefins such as polyethylenes, polypropylenes, polybutylenes, ethylene-propylene copolymers, chlorinated olefin polymers and oxidized ethylene-propylene copolymers.

The aromatic group Ar may have the same structure as any of the aromatic groups Ar discussed below. Examples of the aromatic groups that are useful herein include the polyvalent aromatic groups derived from benzene, naphthalene, anthracene, etc., preferably benzene. Specific examples of Ar groups include phenylenes and naphthylene, e.g., methylphenylenes, ethoxyphenylenes, isopropylphenylenes, hydroxyphenylenes, dipropoxynaphthylenes, etc.

Within this group of aromatic acids, a useful class of carboxylic acids are those of the formula



wherein R_1 is defined above, a is a number in the range of from 1 to about 4, preferably 1 to about 3; b is a number in the range of 1 to about 4, preferably 1 to about 2, c is a number in the range of zero to about 4, preferably 1 to about 2, and more preferably 1; with the proviso that the sum of a, b and c does not exceed 6.

Preferably, b and c are each one and the carboxylic acid is a salicylic acid.

Overbased salts prepared from salicylic acids wherein the aliphatic hydrocarbon based substituents (R_1) are derived from polyalkenes, particularly polymerized lower 1-mono-olefins such as polyethylene, polypropylene, polyisobutylene, ethylene/propylene copolymers and the like and having average carbon contents of about 50 to about 400 carbon atoms are particularly useful.

The above aromatic carboxylic acids are well known or can be prepared according to procedures known in the art. Carboxylic acids of the type illustrated by these formulae and processes for preparing their neutral and basic metal salts are well known and disclosed, for example, in U.S. Patents 2,197,832; 2,197,835; 2,252,662; 2,252,664; 2,714,092; 3,410,798; and 3,595,791. These patents are incorporated by reference for disclosure of carboxylic acids, their basic salts and processes of making the same.

Zinc, calcium and magnesium salts of the aromatic carboxylic acids, and especially the salicylic acids, are preferred.

The sulfonic acids for use in the preparation of component (A) include those represented by the formulas $R^a(SO_3H)_r$ and $(R^b)_xT(SO_3H)_y$. In these formulas, R^a is an aliphatic or aliphatic-substituted cycloaliphatic hydrocarbon or essentially hydrocarbon radical free from acetylenic unsaturation and containing up to about 60 carbon atoms. When R^a is aliphatic, it usually contains at least about 15 carbon atoms; when it is an aliphatic-substituted cycloaliphatic radical, the aliphatic substituents usually contain a total of at least about 12 carbon atoms. Examples of R^a are alkyl, alkenyl and alkoxyalkyl radicals, and aliphatic-substituted cycloaliphatic radicals wherein the aliphatic substituents are alkyl, alkenyl, alkoxy, alkoxyalkyl, carboxyalkyl and the like. Generally, the

cycloaliphatic nucleus is derived from a cycloalkane or a cycloalkene such as cyclopentane, cyclohexane, cyclohexene or cyclopentene. Specific examples of R^a are cetylcyclohexyl, laurylcyclohexyl, cetyloxyethyl, octadecenyl, and radicals derived from petroleum, saturated and unsaturated paraffin wax, and olefin polymers including polymerized monoolefins and diolefins containing about 2-8 carbon atoms per olefinic monomer unit. R^a can also contain other substituents such as phenyl, cycloalkyl, hydroxy, mercapto, halo, nitro, amino, nitroso, lower alkoxy, lower alkylmercapto, carboxy, carbalkoxy, oxo or thio, or interrupting groups such as -NH-, -O- or -S-, as long as the essentially hydrocarbon character thereof is not destroyed.

R^b is generally a hydrocarbon or substantially hydrocarbon radical free from acetylenic unsaturation and containing from about 4 to about 60 aliphatic carbon atoms, preferably an aliphatic hydrocarbon radical such as alkyl or alkenyl. It may also, however, contain substituents or interrupting groups such as those enumerated above provided the essentially hydrocarbon character thereof is retained. In general, any non-hydrocarbon atoms present in R^a or R^b do not account for more than 10% of the total weight thereof. Preferably, R^a and R^b are substantially free of non-hydrocarbon atoms.

The radical T is a cyclic nucleus which may be derived from an aromatic hydrocarbon such as benzene, naphthalene, anthracene or biphenyl, or from a heterocyclic compound such as pyridine, indole or isoindole. Ordinarily, T is an aromatic hydrocarbon nucleus, especially a benzene or naphthalene nucleus.

The subscript x is at least 1 and is generally 1-3. The subscripts r and y have an average value of about 1-4 per molecule, more often about 1.

Illustrative sulfonic acids useful in the preparation of component A are mahogany sulfonic acids,

petrolatum sulfonic acids, mono- and polywax-substituted naphthalene sulfonic acids, cetylchlorobenzene sulfonic acids, cetylphenol sulfonic acids, cetylphenol disulfide sulfonic acids, cetoxycapryl benzene sulfonic acids, dicetyl thianthrene sulfonic acids, dilauryl beta-naphthol sulfonic acids, dicapryl nitronaphthalene sulfonic acids, saturated paraffin wax sulfonic acids, unsaturated paraffin wax sulfonic acids, hydroxy-substituted paraffin wax sulfonic acids, tetraisobutylene sulfonic acids, tetra-amylene sulfonic acids, chloro-substituted paraffin wax sulfonic acids, petroleum naphthene sulfonic acids, cetylcyclopentyl fulsonic acids, lauryl cyclohexyl sulfonic acids, mono- and polywax-substituted cyclohexyl sulfonic acids, postdedecylbenzene sulfonic acids, "dimer alkylate" sulfonic acids, and the like. These sulfonic acids are well-known in the art and require no further discussion herein.

It is desirable that the overbased materials, have a metal ratio of at least about 1.1, preferably at least about 1.5, and more preferably at least 2 to about 4. An especially suitable group of the preferred sulfonic acid and carboxylic acid overbased materials has a metal ratio of at least about 7.0. While overbased materials having a metal ratio of 75 have been prepared, normally the maximum metal ratio will not exceed about 50 and, in most cases, not more than about 40. Especially preferred are those having a metal ratio from about 7 to about 20, except for overbased phenols, wherein the metal ratio generally ranges up to about 10, more often up to about 5.

The overbased materials utilized in the compositions of the invention usually contain from about 10% to about 70% by weight of metal-containing components. The exact nature of these metal-containing components is not known. The remainder of the overbased materials comprise the inert organic reaction medium and any promoter which is

not removed from the overbased product. For purposes of this application, the organic material which is subjected to overbasing is considered a part of the metal-containing components. Normally, the liquid reaction medium constitutes at least about 30% by weight of the reaction mixture utilized to prepare the overbased materials.

In one particularly preferred embodiment, component A is prepared from phenols; that is, compounds containing a hydroxy radical bound directly to an aromatic ring. The term "phenol" as used herein includes compounds having more than one hydroxy group bound to an aromatic ring, such as catechol, resorcinol and hydroquinone. It also includes alkylphenols such as the cresols and ethylphenols, and alkenylphenols. Preferred are phenols containing at least one alkyl or alkenyl substituent containing about 3-100 and especially about 6-50 carbon atoms, such as heptylphenol, octylphenol, dodecylphenol, tetrapropenealkylated phenol, octadecylphenol and polybutenylphenols. Phenols containing more than one substituent may also be used, but the monoalkylphenols are preferred because of their availability and ease of production.

Also useful are condensation products of the above-described phenols with at least one lower aldehyde, the term "lower" denoting aldehydes containing not more than 7 carbon atoms. Suitable aldehydes include formaldehyde, acetaldehyde, propionaldehyde, the butyraldehydes, the valeraldehydes and benzaldehyde. Also suitable are aldehyde-yielding reagents such as paraformaldehyde, trioxane, methylol, Methyl Formcel and paraldehyde. Formaldehyde and the formaldehyde-yielding reagents are especially preferred.

In a particularly preferred embodiment, the metal phenates are overbased metal phenates, more preferably overbased sulfurized metal phenates, preferably alkaline earth metal phenates, and especially calcium phenates.

The phenol group of the phenates includes an aromatic moiety with at least one hydrocarbon-based radical and an oxygen atom attached to such aromatic moiety, as indicated in Formula I, below. The phenol group may be sulfurized and reacted with a metal, as discussed below, to form component (A). As used herein, the term "normal" metal phenates is used to refer to those phenates wherein the ratio of equivalents of metal to the phenolic O group is about 1:1, in accordance with Formula I

$$(R_a - Ar - O -)_x M \qquad \text{I}$$

wherein $(R_a - Ar - O-)$ is the phenol group; M is a metal; x is the valence of M. Ar is an aromatic moiety which is preferably benzene; R is a hydrocarbon-based radical; and a is an integer of from 1 up to the number of unsatisfied valences in Ar, preferably 1 or 2. As used herein, the term overbased metal phenates refers to metal phenates wherein the ratio of metal to the phenol group is greater than that of normal metal phenates. Such phenates are sometimes referred to interchangeably as "basic" or "overbased". Component (A) generally contains up to about 1000%, preferably up to about 500%, of the metal present in the corresponding normal metal phenate. Advantageously, component (A) contains from about 250% to about 450%, preferably up to about 350%, of the metal present in the corresponding normal metal phenate.

Any of alkali or alkaline earth metals, copper or zinc may be used in the phenate of component (A); however, alkaline earth metal compounds are preferred, and calcium is especially preferred.

As mentioned hereinabove, component (A) preferably comprises a sulfurized metal phenate and the metal contents referred to hereinabove apply equally to this preferred embodiment. When component (A) is a sulfurized phenate it has a phenol to sulfur group molar ratio of from about 2:1 to about 1:2, preferably about 2:1 to about 1:1, and advantageously about 4:3.

The term "basic" is used herein the same way in which it was used in the definition of other components above, that is, it refers to salts having a metal ratio in excess of 1. The neutral and basic salts of phenol sulfides provide antioxidant and detergent properties to the oil compositions of the invention.

In a particularly preferred embodiment, component (A) includes, for example, basic sulfurized tetrapropenyl phenate with, for example, about 230% or 380% of the calcium present in the corresponding normal calcium phenate, and a phenol to sulfur group molar ratio of about 4:3.

The alkylphenols from which the neutral and overbased salts are prepared generally comprise phenols containing hydrocarbon substituents with at least about 6 carbon atoms; the substituents may contain up to about 700 aliphatic carbon atoms. Also included are substantially hydrocarbon substituents, as defined hereinabove. The preferred hydrocarbon substituents are derived from the polymerization of olefins such as ethylene, propene, etc.

The term "alkylphenol sulfides" is meant to include di-(alkylphenol)monosulfides, disulfides, polysulfides, and other products obtained by the reaction of the alkylphenol with sulfur monochloride, sulfur dichloride or elemental sulfur. The molar ratio of the phenol to the sulfur compound can be, depending on the sulfur compound, from about 1:0.5 to about 1:1.5, or higher. For example, phenol sulfides are readily obtained by mixing, at a temperature above about 60°C, one mole of an alkylphenol and about 0.5-1 mole of sulfur dichloride. The reaction mixture is usually maintained at about 100°C for about 2-5 hours, after which time the resulting sulfide is stripped of volatiles and filtered. When elemental sulfur is used, temperatures of about 200°C or higher are sometimes desirable. It is also desirable

that the drying operation be conducted under nitrogen or a similar inert gas.

A commonly employed method for preparing the basic (or overbased) salts of these phenols comprises heating the phenol with a stoichiometric excess of a metal neutralizing agent such as a metal oxide, hydroxide, carbonate, bicarbonate, sulfide, etc., at temperatures above about 50°C. Various promoters may be used in the overbasing process to aid in the incorporation of the excess metal. Promoters include such compounds as phenolic substances including phenol; alcohols such as methanol, 2-propanol, octyl alcohol, etc.; amines such as aniline and dodecyl amine, etc. Preferably, the basic salt is treated with carbon dioxide after it has been formed. The techniques of overbasing various phenols are described in the prior art and can be utilized as processes for preparing the basic or overbased phenols used in the present invention.

The preparation of sulfurized metal phenates is also well known to those skilled in the art. Neutral salts are prepared by mixing and heating a basic metal compound with the desired phenol compound.

The preparation of basic (overbased) phenates can be accomplished by any of the standard techniques known to those skilled in the art for producing basic sulfurized metal phenates. These techniques include, for example, one-step processes wherein sulfurization and basing (or overbasing) with the metal are effected simultaneously, and two-step processes wherein the phenol is first sulfurized, forming an alkylphenol sulfide, then based. Each of these techniques is well known to those skilled in the art and, accordingly, need not be further discussed herein. The source of sulfur is generally elemental sulfur, or sulfur halide, for example, SCl_2 or S_2Cl_2. Patents disclosing suitable procedures for preparing component (B) include U.S. Pat. Nos. 2,680,096;

3,036,971; 3,178,368; 3,437,595; and Re 29,661, these patents being incorporated herein by reference.

Suitable basic alkyl phenol sulfides are disclosed, for example, in U.S. Pat. Nos. 3,372,116, 3,410,798 and 3,562,159, 4,021,419 and 4,740,321 which are hereby incorporated by reference.

The metal salts, component (A), are generally employed in the compositions of this invention in amounts ranging from about 0.1 to about 10% by weight of the total lubricating oil composition. More often, they are used in amounts ranging from about 0.02 to about 5%, frequently up to about 2% and preferably from about 0.04% to about 1% by weight of the lubricating compositions.

The following examples illustrate the preparation of metal salts useful as component (A). All temperatures are in degrees Celsius, all parts are parts by weight unless indicated otherwise. These examples are intended to be illustrative only, and are not intended to be construed as limiting the scope of this invention.

Examples A-1 through A-10 are non-limiting examples of the preparation of metal carboxylates, sulfonates and mixtures thereof.

Example A-1

To 790 parts of an oil solution containing 1 equivalent based on neutralization number of an alkylated benzenesulfonic acid and 71 parts of polybutenyl succinic anhydride (equivalent weight about 560) containing predominantly isobutene units in 176 parts of mineral oil is added 320 parts (8 equivalents) of sodium hydroxide and 640 parts (20 equivalents) of methanol. The temperature of the mixture increases to 89°C (reflux) over 10 minutes due to exotherming. During this period, the mixture is blown with carbon dioxide at 4 cfh (cubic feet per hour). Carbonation is continued for about 30 minutes as the temperature gradually decreases to 74°C. The methanol and other volatile materials are stripped

from the carbonated mixture by blowing nitrogen through it at 2 cfh while the temperature is slowly increased to 150°C over 90 minutes. After stripping is completed, the remaining mixture is held at 155°C-165°C for about 30 minutes and filtered to yield an oil solution of the desired basic sodium sulfonate having a metal ratio of about 7.75.

Example A-2

Following the procedure of Example A-1, a solution of 780 parts (1 equivalent) of an alkylated benzenesulfonic acid (57% by weight 100 neutral mineral oil and unreacted alkylated benzene) and 119 parts of the polybutenyl succinic anhydride in 442 parts of mineral oil is mixed with 800 parts (20 equivalents) of sodium hydroxide and 704 parts (22 equivalents) of methanol. The mixture is blown with carbon dioxide at 7 cfh for 11 minutes as the temperature slowly increases to 97°C. The rate of carbon dioxide flow is reduced to 6 cfh and the temperature decreases slowly to 88°C over about 40 minutes. The rate of carbon dioxide flow is reduced to 5 cfh for about 35 minutes and the temperature slowly decreases to 73°C. The volatile materials are stripped by blowing nitrogen through the carbonated mixture at 2 cfh for 105 minutes as the temperature is slowly increased to 160°C. After stripping is completed, the mixture is held at 160°C for an additional 45 minutes and then filtered to yield an oil solution of the desired basic sodium sulfonate having a metal ratio of about 19.75.

Example A-3

A mixture of 906 parts of an oil solution of an alkyl phenyl sulfonic acid (having a molecular weight of 450), 564 parts mineral oil, 600 parts toluene, 98.7 parts magnesium oxide and 120 parts water is blown with carbon dioxide at a temperature of 78°-85°C for 7 hours at a rate of about 3 cubic feet of carbon dioxide per

hour. The reaction mixture is constantly agitated throughout the carbonation. After carbonation, the reaction mixture is stripped to 165°C/20 torr and the residue filtered. The filtrate is an oil solution (34% oil) of the desired overbased magnesium sulfonate having a metal ratio of about 3.

Example A-4

A polybutenyl succinic anhydride is prepared by reacting a chlorinated polybutene (having an average chlorine content of 4.3% and derived from a polybutene consisting predominantly of isobutene units having a number average molecular weight of about 1150) with maleic anhydride at about 200°C. To a mixture of 1246 parts of this succinic anhydride and 1000 parts of toluene there is added at 25°C, 76.6 parts of barium oxide. The mixture is heated to 115°C and 125 parts of water is added drop-wise over a period of one hour. The mixture is then allowed to reflux at 150°C until all the barium oxide is reacted. Stripping and filtration provides a filtrate containing the desired product.

Example A-5

A basic calcium sulfonate having a metal ratio of about 15 is prepared by carbonation, in increments, of a mixture of calcium hydroxide, a neutral sodium petroleum sulfonate, calcium chloride, methanol and an alkyl phenol, followed by removal of volatile materials and filtration of the residue.

Example A-6

A mixture of 323 parts of mineral oil, 4.8 parts of water, 0.74 parts of calcium chloride, 79 parts of lime, and 128 parts of methyl alcohol is prepared, and warmed to a temperature of about 50°C. To this mixture there is added 1000 parts of an alkyl phenyl sulfonic acid having a molecular weight of 500 with mixing. The mixture then

is blown with carbon dioxide at a temperature of about 50°C at a rate of about 5.4 pounds per hour for about 2.5 hours. After carbonation, 102 additional parts of oil are added and the mixture is stripped of volatile materials at a temperature of about 150-155°C at 55 mm. pressure. The residue is filtered and the filtrate is the desired oil solution of the overbased calcium sulfonate having calcium content of about 3.7% and a metal ratio of about 1.7.

Example A-7

A mixture of 490 parts (by weight) of a mineral oil, 110 parts of water, 61 parts of heptylphenol, 340 parts of barium mahogany sulfonate, and 227 parts of barium oxide is heated at 100°C for 0.5 hour and then to 150°C. Carbon dioxide is then bubbled into the mixture until the mixture is substantially neutral. The mixture is filtered and the filtrate found to have a sulfate ash content of 25%.

Example A-8

Add to a flask about 512 parts by weight of a mineral oil solution containing about 0.5 equivalent of a substantially neutral magnesium salt of an alkylated salicylic acid wherein the alkyl group has an average of about 18 aliphatic carbon atoms, about 30 parts by weight of an oil mixture containing about 0.037 equivalent of an alkylated benzenesulfonic acid together with about 15 parts by weight (0.65 equivalents) of magnesium oxide and about 250 parts by weight of xylene. Heat to a temperature of about 60°C to 70°C. Increase the heat to about 85°C and add approximately 60 parts by weight of water. Hold the reaction mass at a reflux temperature of about 95°C to 100°C for about 1 1/2 hours and subsequently strip at a temperature of 155-160°C, under a vacuum, and filter. The filtrate will comprise the basic

carboxylic magnesium salt containing 200% of the stoichiometrically equivalent amount of magnesium.

Example A-9

Prepare a substantially neutral magnesium salt of an alkylated salicylic acid wherein the alkyl groups have from 16 to 24 aliphatic carbon atoms by reacting approximately stoichiometric amounts of magnesium chloride with a substantially neutral potassium salt of the alkylated salicylic acid. Charge a flask with a reaction mass comprising approximately 6580 parts by weight of a mineral oil solution containing about 6.50 equivalents of the substantially neutral magnesium salt of the alkylated salicylic acid and about 388 parts by weight of an oil mixture containing about 0.48 equivalent of an alkylated benzenesulfonic acid together with approximately 285 parts by weight (14 equivalents) of magnesium oxide and approximately 3252 parts by weight of xylene. Heat to a temperature of about 55°C to 75°C. Increase the temperature to about 82°C and add approximately 780 parts by weight of water to the reaction and then heat to the reflux temperature. Hold the reaction mass at the reflux temperature of about 95-100°C for about one hour and subsequently strip at a temperature of about 170°C, under 50 torr and filter. The filtrate will comprise the basic carboxylic magnesium salts and have a sulfated ash content of 15.7% (sulfated ash) corresponding to 276% of the stoichiometrically equivalent amount.

Example A-10

A reaction mixture comprising 2900 grams (3 equivalents) of an oil solution of the magnesium salt of polyisobutylene (average molecular weight--480)-substituted salicyclic acids, 624 grams of mineral oil, 277 grams (1 equivalent) of a commercial mixture of tall oil acids, 1800 grams of xylene, 195 grams (9

equivalents) of magnesium oxide, and 480 grams of water are carbonated at the reflux temperature (about 95°C) for one hour. The carbonated mixture is then stripped by first heating to 160°C with nitrogen blowing (3 cubic feet per hour) and thereafter heating to 165°C at a pressure of 30 mm. (Hg). This stripped carbonated product is filtered, the filtrate being an oil solution of the desired basic magnesium salt. The salt is characterized by a metal ratio of 2.7.

The following examples A-11 through A-15 illustrate the preparation of phenol salts.

Example A-11

A phenol sulfide is prepared by reacting sulfur dichloride with a polyisobutenyl phenol in which the polyisobutenyl substituent has an average of 23.8 carbon atoms, in the presence of sodium acetate (an acid acceptor used to avoid discoloration of the product). A mixture of 1755 parts of this phenol sulfide, 500 parts of mineral oil, 335 parts of calcium hydroxide and 407 parts of methanol is heated to about 43-50°C and carbon dioxide is bubbled through the mixture for about 7.5 hours. The mixture is then heated to drive off volatile matter, an additional 422.5 parts of oil are added to provide a 60% solution in oil. This solution contains 5.6% calcium and 1.59% sulfur.

Example A-12

To 6072 parts (22 moles OH) of a tetrapropenyl-substituted phenol (prepared by mixing, at 138°C and in the presence of a sulfuric acid treated clay, phenol and tetrapropylene), there are added at 90°-95°C, 1134 parts (11 moles) of sulfur dichloride. The addition is made over a 4-hour period whereupon the mixture is bubbled with nitrogen for 2 hours, heated to 150°C and filtered. To 861 parts (3 equivalents) of the above product, 1068 parts of mineral oil, and 90 parts of water, there are

added at 70°C, 122 parts (3.3 equivalents) of calcium hydroxide. The mixture is maintained at 110°C for 2 hours, heated to 165°C and maintained at this temperature until it is dry. Thereupon, the mixture is cooled to 25°C and 180 parts of methanol are added. The mixture is heated to 50°C and 366 parts (9.9 equivalents) of calcium hydroxide and 50 parts (0.633 equivalent) of calcium acetate are added. The mixture is agitated for 45 minutes and is then treated at 50-70°C with carbon dioxide at a rate of 2-5 cubic feet per hour for 3 hours. The mixture is dried at 165°C and the residue is filtered. The filtrate has a calcium content of 3.3%, a neutralization number of 39 (basic) and a metal ratio of 4.4.

Example A-13

To 5880 parts (12 moles OH) of a polyisobutene-substituted phenol (prepared by mixing, at 54°C and in the presence of boron trifluoride, equimolar amounts of phenol and a polyisobutene having a number average molecular weight of about 350) and 2186 parts of mineral oil, there are added over 2.5 hours and at 90-110°C, 618 parts (6 moles) of sulfur dichloride. The mixture is heated to 150°C and bubbled with nitrogen. To 3449 parts (5.25 equivalents) of the above product, 1200 parts of mineral oil, and 130 parts of water, there are added at 70°C, 147 parts (5.25 equivalents) of calcium oxide. The mixture is maintained at 95-110°C for 2 hours, heated to and maintained at 160°C for one hour and then cooled to 60°C whereupon 920 parts of 1-propanol, 307 parts (10.95 equivalents) of calcium oxide, and 46.3 parts (0.78 equivalent) of acetic acid are added. The mixture is then contacted with carbon dioxide at a rate of 2 cubic feet per hour for 2.5 hours. The mixture is dried at 190°C and the residue is filtered to give the desired product.

Example A-14

A mixture of 485 parts (1 moles OH) of a polyisobutene-substituted phenol wherein the substituent has a number average molecular weight of about 400, 32 parts (1 equivalent) of sulfur, 111 parts (3 equivalents) of calcium hydroxide, 16 parts (0.2 equivalent) of calcium acetate, 485 parts of diethylene glycol monomethyl ether and 414 parts of mineral oil is heated at 120-205°C under nitrogen for 4 hours. Hydrogen sulfide evolution begins as the temperature rises above 125°C. The material is allowed to distill and hydrogen sulfide is absorbed in a sodium hydroxide solution. Heating is discontinued when no further hydrogen sulfide absorption is noted; the remaining volatile material is removed by distillation at 95°C/10 mm pressure. The distillation residue is filtered. The product thus obtained is a 60% solution of the desired product in mineral oil.

Example A-15

To a mixture of 3192 parts (12 equivalents) of tetrapropenyl-substituted phenol, 2400 parts of mineral oil and 465 parts (6 equivalents) of 40% aqueous formaldehyde at 82°C, is added, over 45 minutes, 960 parts (12 equivalents) of 50% aqueous sodium hydroxide. Volatile materials are removed by stripping at 160°C under nitrogen and subsequently under vacuum, and to the residue is added 618 parts (12 equivalents) of sulfur dichloride over 3 hours. Toluene, 1000 parts, and 1000 parts of water are added and the mixture is heated under reflux for 2 hours. Volatile materials are then removed at 180°C by blowing with nitrogen and the intermediate is filtered.

To 1950 parts (4 equivalents) of the intermediate thus obtained is added 135 parts of the polybutenyl succinic anhydride wherein the polybutenyl group has a molecular weight of about 1000 and consists primarily of

isobutene units. The mixture is heated to 51°C, and 78 parts of acetic acid and 431 parts of methanol are added, followed by 325 parts (8.8 equivalents) of calcium hydroxide. The mixture is blown with carbon dioxide and is finally stripped with nitrogen blowing at 158°C and filtered while hot, using a filter aid. The filtrate is a 68% solution in mineral oil of the desired product and contains 2.63% sulfur and 22.99% calcium sulfate ash.

The Carboxylic Acid or Anhydride

Component (B) is an aliphatic carboxylic acid or an anhydride thereof, wherein the aliphatic group contains at least about 20 carbon atoms and up to about 500 carbon atoms, preferably from about 30 to about 300 carbon atoms and often from about 30 to about 150 carbon atoms. In another embodiment, component (B) is an aliphatic substituted succinic anhydride or acid containing from about 20 to about 500 carbon atoms in the aliphatic substituent, preferably from about 30 to about 400 carbon atoms, and often from about 50 to about 200 carbon atoms. Patents describing useful aliphatic carboxylic acids or anhydrides and methods for preparing them include, among numerous others, U.S. Pat. Nos. 3,215,707 (Rense); 3,219,666 (Norman et al), 3,231,587 (Rense); 3,912,764 (Palmer); 4,110,349 (Cohen); and 4,234,435 (Meinhardt et al); and U.K. 1,440,219.

As indicated in the above-mentioned patents, which are hereby incorporated by reference for their disclosure of compounds useful as component (B) of this invention, the carboxylic acids (or various derivatives thereof) are usually derived by the reaction of a carboxylic acid containing compound with a polyalkene or halogenated derivative thereof or a suitable olefin.

The polyalkenes from which the carboxylic acids (B) are derived are homopolymers and interpolymers of polymerizable olefin monomers of 2 to about 16 carbon atoms; usually 2 to about 6 carbon atoms. The

interpolymers are those in which two or more olefin monomers are interpolymerized according to well-known conventional procedures to form polyalkenes having units within their structure derived from each of said two or more olefin monomers. Thus, "interpolymer(s)" as used herein is inclusive of copolymers, terpolymers, tetrapolymers, and the like. As will be apparent to those of ordinary skill in the art, the polyalkenes from which the substituent groups are derived are often conventionally referred to as "polyolefin(s)".

The olefin monomers from which the polyalkenes are derived are polymerizable olefin monomers characterized by the presence of one or more ethylenically unsaturated groups (i.e., >C=C<); that is, they are monolefinic monomers such as ethylene, propylene, butene-1, isobutene, and octene-1 or polyolefinic monomers (usually diolefinic monomers) such as butadiene-1,3 and isoprene.

These olefin monomers are usually polymerizable terminal olefins; that is, olefins characterized by the presence in their structure of the group >C=CH_2. However, polymerizable internal olefin monomers (sometimes referred to in the literature as medial olefins) characterized by the presence within their structure of the group

-C-C=C-C-

can also be used to form the polyalkenes. When internal olefin monomers are employed, they normally will be employed with terminal olefins to produce polyalkenes which are interpolymers. For purposes of this invention, when a particular polymerized olefin monomer can be classified as both a terminal olefin and an internal olefin, it will be deemed to be a terminal olefin. Thus, 1,3-pentadiene (i.e., piperylene) is deemed to be a terminal olefin for purposes of this invention.

Preferred carboxylic acids include polyolefin substituted succinic acids, succinic anhydrides, ester acids or lactone acids.

Component (B) is generally used in the lubricating oil compositions of this invention in amounts ranging from about 0.01% to about 10% by weight of the lubricating oil composition, preferably from about 0.01% to about 5% by weight and often up to about 1% by weight. Most preferably, component (B) is present in amounts ranging from about 0.02% to about 1% by weight.

Non-limiting examples of compounds useful as component (B) include those in the following examples:

Example B-1

A mixture of 6400 parts (4 moles) of a polybutene comprising predominantly isobutene units and having a molecular weight of about 1600 and 408 parts (4.16 moles) of maleic anhydride is heated at 225-240°C for 4 hours. It is then cooled to 170°C and an additional 102 parts (1.04 moles) of maleic anhydride is added, followed by 70 parts (0.99 mole) of chlorine; the latter is added over 3 hours at 170-215°C. The mixture is heated for an additional 3 hours at 215°C and is then vacuum stripped at 220°C and filtered through diatomaceous earth. The product is the desired polybutenyl-substituted succinic anhydride having a saponification number of 61.8.

Example B-2

A monocarboxylic acid is prepared by chlorinating a polyisobutene having a molecular weight of 750 to a product having a chlorine content of 3.6% by weight, converting the product to the corresponding nitrile by reaction with an equivalent amount of potassium cyanide in the presence of a catalytic amount of cuprous cyanide and hydrolyzing the resulting nitrile by treatment with 50% excess of a dilute aqueous sulfuric acid at the reflux temperature.

Example B-3

A high molecular weight mono-carboxylic acid is prepared by telomerizing ethylene with carbon tetrachloride to a telomer having an average of 35 ethylene radicals per molecule and hydrolyzing the telomer to the corresponding acid in according with the procedure described in British Patent No. 581,899.

Example B-4

A polybutenyl succinic anhydride is prepared by the reaction of a chlorinated polybutylene with maleic anhydride at 200°C. The polybutenyl radical has an average molecular weight of 805 and contains primarily isobutene units. The resulting alkenyl succinic anhydride is found to have an acid number of 113 (corresponding to an equivalent weight of 500).

Example B-5

A lactone acid is prepared by reacting 2 equivalents of a polyolefin (Mn about 900) substituted succinic anhydride with 1.02 equivalents of water at a temperature of about 90°C in the presence of a catalytic amount of concentrated sulfuric acid. Following completion of the reaction, the sulfuric acid catalyst is neutralized with sodium carbonate and the reaction mixture is filtered.

Example B-6

An ester acid is prepared by reacting 2 equivalents of an alkyl substituted succinic anhydride having an average of about 35 carbon atoms in the alkyl group with 1 mole of ethanol.

Example B-7

A reactor is charged with 1000 parts of polybutene having a molecular weight determined by vapor phase isometry of about 950 and which consists primarily of isobutene units, followed by the addition of 108 parts of moleic anhydride. The mixture is heated to 110°C

followed by the sub-surface addition of 100 parts Cl_2 over 6.5 hours at a temperature ranging from 110 to 188°C. The exothermic reaction is controlled as not to exceed 188°C. The batch is blown with nitrogen then stored.

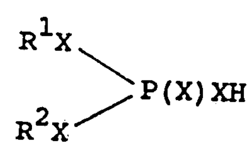
Example B-8

The procedure of Example B-7 is repeated employing 1000 parts of polybutene having a molecular weight determined by vapor phase isometry of about 1650 and consisting primarily of isobutene units and 106 parts moleic anhydride. Cl_2 is added beginning at 130°C and added a near continuous rate such that the maximum temperature of 188°C is reached near the end of chlorination. The residue is blown with nitrogen and collected.

(C) The Metal Salts of an Organic Phosphorus Acid or Mixture of Organic Phosphorus Acid and Carboxylic Acid

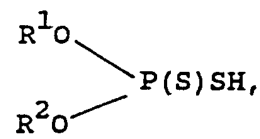
The compositions of the present invention may also contain (C) a metal salt of (C)(I) at least one organic phosphorus acid or mixture of (C)(I) at least one organic phosphorus acid and (C)(II) at least one carboxylic acid.

The phosphorus acid (B)(I) is preferably at least one acid of the general formula



wherein R^1 and R^2 is the same or different and each of R^1 and R^2 is independently H or a hydrocarbon-based group with the proviso that at least one of R^1 and R^2 is a hydrocarbon-based group and each X is independently S or O.

In a preferred embodiment, the phosphorus acid (C)(I) has the general formula



wherein R^1 and R^2 are as defined hereinabove. These are referred to as phosphorodithioic acids.

The hydrocarbon-based groups R^1 and R^2 may be alkyl, cycloalkyl, aralkyl or alkaryl groups. Illustrative alkyl groups include isopropyl, isobutyl, n-butyl, sec-butyl, the various amyl groups, n-hexyl, ethylisobutyl carbinyl, heptyl, 2-ethylhexyl, diisobutyl, isooctyl, nonyl, behenyl, decyl, dodecyl, tridecyl, etc. Illustrative alkaryl groups include lower alkylphenyl groups such as butylphenyl, amylphenyl, heptylphenyl, etc. Cycloalkyl groups likewise are useful and these include chiefly cyclohexyl and the lower alkyl-cyclohexyl radicals. Lower alkyl groups contain from one to about seven carbon atoms. Many substituted hydrocarbon groups may also be used, e.g., chloropentyl, dichlorophenyl, and dichlorodecyl.

The preparation of these acids is well known in the art and is described in the patent literature and numerous other texts and publications. See for example the books, "Lubricant Additives," by C. V. Smalheer and R. K. Smith, published by Lezius-Hiles Co., Cleveland, Ohio (1967) and "Lubricant Additives," by M. W. Ranney, published by Noyes Data Corp., Parkridge, New Jersey (1973), and the following U.S. Patents:

2,261,047	3,211,648	3,402,188
2,540,084	3,211,649	3,413,327
2,838,555	3,213,020	3,446,735
2,861,907	3,213,021	3,502,677
2,862,947	3,213,022	3,573,292
2,952,699	3,305,598	3,859,300
2,987,410	3,328,298	4,002,686

3,004,996	3,335,158	4,089,793
3,089,867	3,376,221	4,123,370
3,151,075	3,390,082	4,308,154
3,190,833	3,401,185	4,466,895
		4,507,215

These books and patents are hereby incorporated by reference for relevant disclosures contained therein.

Preferred acids of the general formula

$$\begin{matrix} R^1O \diagdown \\ \qquad P(S)(S)H \\ R^2O \diagup \end{matrix}$$

are readily obtainable from the reaction of phosphorus pentasulfide (P_2S_5) with an alcohol or mixtures of alcohols. The reaction involves mixing at a temperature of about 20°C to about 200°C, 4 moles of the alcohol with one mole of phosphorus pentasulfide. Hydrogen sulfide is liberated in this reaction. The oxygen-containing analogs of these acids are conveniently prepared by treating the dithioic acid with water or steam which, in effect, replaces one or both of the sulfur atoms.

The mixed phosphates $(RO)_x\overset{\overset{O}{\|}}{P}(OH)_y$ are readily prepared by reacting 3 moles of an alcohol with 1 mole of phosphorus pentoxide (P_2O_5).

The expression "hydrocarbon-based group" as used herein with respect to R^1 and R^2 is used to define a monovalent radical derived from a hydrocarbon-based material by removal of a hydrogen from a carbon atom of the hydrocarbon-based material. This carbon atom is directly bonded to the remainder of the molecule. The hydrocarbon-based groups may be straight chains, e.g., isopropyl-, n-pentyl, sec-butyl-, etc. or branched, e.g., 2-methyl-4-pentyl-, isooctyl-, etc.

Preferably the groups R^1 and R^2 are substantially saturated. The terminology "substantially saturated" as used herein is intended to define radicals free from acetylenic unsaturation (-C C-) in which there is not more than one ethylenic linkage (-C=C-) for every 10 carbon-to carbon (preferably 20) covalent bonds. The so-called "double bonds" in aromatic rings (e.g., benzene) are not to be considered as contributing to unsaturation with respect to the terminology "substantially saturated". Usually there will be no more than an average of one ethylenic linkage per substantially saturated monovalent radical as described hereinbefore. Preferably, (with the exception of aromatic rings) all the carbon-to-carbon bonds in a substantially saturated radical will be saturated linkages; that is, the radical will be free from acetylenic and ethylenic linkages. For the purposes of this disclosure, aromatic unsaturation is not to be considered ethylenic unsaturation.

In general, the hydrocarbon-based radical may contain at least 3 carbon atoms and up to about 100 carbon atoms with a preferred range from 3 to about 50 carbon atoms, more preferably from about 3 to about 16 carbon atoms. Other preferred ranges are from about 6 to about 18 carbons, more preferably from about 6 to about 8 carbons. Mixtures wherein R^1 and R^2 are different are useful. Typical examples of R and R^1 include isopropyl-, n-butyl-, n-pentyl-, 4-methyl-2-pentyl-, isooctyl-, n-dodecyl-, etc. Mixtures, such as isopropyl- and isooctyl, sec-butyl and n-decyl-, isopropyl- and 4-methyl-2-pentyl- and the like are useful. Mixtures are often statistical mixtures which comprise a mixture wherein some of the molecules have both R^1 and R^2 alike and additional molecules wherein R^1 and R^2 are different.

The term "lower" when used herein to denote radicals such as lower alkyl is intended to describe a radical containing up to about 7 carbon atoms.

Methods for preparing the metal salts (C) are well known and are described in detail in the patent literature. Most frequently, the salts are prepared by reacting one or more of the phosphorus-containing acids described hereinabove with a metal base. Suitable metal bases include the free metals previously enumerated and their oxides, hydroxides, alkoxides and basic salts. Examples include sodium hydroxide, calcium hydroxide, zinc oxide, copper oxide, calcium acetate and the like. Other methods include "double-displacement" reactions wherein one metal salt of a phosphorus acid is reacted with a salt, such as a halide, of another metal. Metal exchange may take place. For example, a sodium dithiophosphate can be reacted with calcium chloride to form a calcium dithiophosphate and sodium chloride. Sodium chloride is then removed by means commonly used in the art, such as filtration, water washing, etc. These and other methods are described in the books and U.S. Patents listed hereinabove which describe the method of preparation of the various phosphorus acids. Each of the above-listed books and patents is hereby incorporated by reference for disclosures relating to the preparation of the metal salts.

Also contemplated for use in the lubricating compositions of this invention are metal salts of phosphorus-containing acids as described hereinabove, which have been post-treated with other reagents to improve various properties. Examples include post-treatments with phosphites, epoxides, amines and the like. Such post-treatments and products so obtained are described in the following U.S. Patents:

3,004,996	3,213,022
3,151,075	3,213,023
3,211,648	4,263,150
3,211,649	4,289,635
3,213,020	4,507,215
3,213,021	

As noted hereinabove, the metal salts (C) useful in the lubricating compositions of this invention may be metal salts of a mixture of (C)(I) at least one organic phosphorus acid and (C)(II) at least one carboxylic acid wherein the various elements of the formula are as described hereinabove.

These metal salts are salts of at least two acidic components. The phosphorus-containing acids (C)(I) have been described hereinabove.

The carboxylic acid reactant (C)(II) may be a monocarboxylic or polycarboxylic acid, usually containing from 1 to about 3 carboxy groups and preferably only 1. It may contain from about 2 to about 40, preferably from about 2 to about 20 carbon atoms. The preferred carboxylic acids are those having the formula R^3COOH, wherein R^3 is an aliphatic or alicyclic hydrocarbon-based group preferably free from acetylenic unsaturation. Suitable acids include acetic, propionic, butanoic, hexanoic, decanoic, dodecanoic, octadecanoic and eicosanoic acids, as well as olefinic acids such as acrylic, oleic, linoleic, and linoleic acid dimer. For the most part, R^3 is a saturated aliphatic radical and especially a branched alkyl radical such as the isopropyl or 3-heptyl radical. Illustrative polycarboxylic acids are oxalic, malonic, succinic, alkyl- and alkenylsuccinic, glutaric, adipic, pimelic, sebacic, maleic, fumaric and citric acids.

The salt of a mixture of (C)(I) and (C)(II) may be prepared by merely blending a metal salt of compoment

(C)(I) with a metal salt of component (C)(II) in the desired ratio. This ratio is between about 0.5:1 and about 500:1 on an equivalent basis. Preferably, the ratio is between about 0.5:1 and about 200:1. Advantageously, the ratio can be from about 0.5:1 to about 100:1, preferably from about 0.5:1 to about 50:1, and more preferably from about 0.5:1 to about 20:1. Further, the ratio can be from about 0.5:1 to about 4.5:1, preferably about 2.5:1 to about 4.25:1. For this purpose, the equivalent weight of a phosphorus containing acid (C)(I) is its molecular weight divided by the number of acidic groups, and that of a carboxylic acid is its molecular weight divided by the number of carboxy groups therein. The information required to determine equivalents can usually be determined from the structural formula of components (C)(I) and (C)(II) or empirically through well-known titration procedures.

A second and preferred method for preparing the metal salts of mixtures of acids (C)(I) and (C)(II) is to prepare a mixture of the acids in the desired ratio and to react the acid mixture with a suitable metal base. When this method of preparation is used, it is frequently possible to prepare a neutral salt or a salt containing an excess of metal with respect to the number of equivalents of acid present; thus, mixed metal salts containing as many as 2 equivalents and especially up to about 1.5 equivalents of metal per equivalent of acid may be prepared. The equivalent of a metal for this purpose is its atomic weight divided by its valence.

The term "neutral salt" refers to salts characterized by metal content equal to that which would be present according to the stoichiometry of the metal and the particular organic compound reacted with the metal. Thus, if a phosphorodithioic acid, $(RO)_2PSSH$, is neutralized with a basic metal compound, e.g., zinc oxide, the neutral metal salt produced would contain one

equivalent of zinc for each equivalent of acid, i.e., $[(RO)_2PSS]_2Zn$.

However, component (C) can contain more or less than the stoichiometric amount of metal. The products containing less than the stoichiometric amount of metal are acidic materials. The products containing more than the stoichiometric amount of metal are overbased materials. Component (C) may have about 80% to about 200%, preferably about 100% to about 150%, more preferably about 100% to about 135%, and advantageously about 103% to about 110% of the metal present in the corresponding neutral salt.

Variants of the above-described methods may also be used to prepare the mixed metal salts of this invention. For example, a metal salt, component (C) may be blended with the free acid as component (C)(II), and the resulting blend reacted with additional metal base.

Suitable metal bases for the preparations of the metal salts (C) of this invention include the free metals previously enumerated and their oxides, hydroxides, alkoxides and basic salts. Examples are sodium hydroxide, sodium methoxide, sodium carbonate, potassium hydroxide, potassium carbonate, magnesium oxide, magnesium hydroxide, calcium hydroxide, calcium acetate, zinc oxide, zinc acetate, lead oxide, nickel oxide, copper oxide, antimony trioxide and the like.

The temperature at which the metal salts used in this invention are prepared is generally between about 30°C and about 150°C, preferably up to about 125°C. If component (C) is prepared by neutralization of a mixture of acids with a metal base, it is preferred to employ temperatures above about 50°C and especially above about 75°C. It is frequently advantageous to conduct the reaction in the presence of a substantially inert, normally liquid organic diluent such as naphtha, benzene, xylene, mineral oil or the like. If the diluent is mineral oil or is physically and chemically similar to

mineral oil, it frequently need not be removed before using component (C) in the compositions of the invention.

Component (C), when present, is generally used in the lubricating oil compositions of this invention in amounts ranging up to about 10% of the total weight of the lubricating oil composition. More often, component (C), when used, is present in amounts ranging from about 0.05% to about 5%, preferably from about 0.1 to about 2% and more preferably from about 0.1 to about 1% by weight of the lubricating oil composition.

As mentioned hereinabove, and as illustrated by the numerous references incorporated herein which describe the metal salts of phosphorus-containing acids, the metal salts and derivatives thereof are well known in the art. The following examples are provided to illustrate several of the metal salts useful as component (C) in this invention. It is emphasized that these examples are provided for illustrative purposes and are not to serve as a limitation on the scope of the invention.

Example (C-1)

One mole of an O,O-di(alkyl)phosphorodithioic acid containing 40 mole % isopropyl and 60 mole % 4-methyl-2-pentyl group is reacted with an oil slurry of 1.08 equivalents (0.54 moles) of zinc oxide at about 190°F (88°C). H_2O is evolved. The reaction mixture is steam stripped followed by vacuum stripping. Oil is added if necessary to adjust the phosphorus content of the residue to about 9.5%. The oil solution is filtered.

Example (C-2)

The procedure of Example B-1 is repeated employing 1 mole of di(4-methyl-2-pentyl)dithiophosphoric acid and 1.1 equivalents (0.55 moles) of an oil slurry of zinc oxide. The filtered product contains 8.5% phosphorus.

Example (C-3)

The procedure of Example B-2 is repeated except no oil diluent is employed. The filtered product contains 9.25% phosphorus.

Example (C-4)

A mixture of 67 parts (1.63 equivalents) of zinc oxide and 48 parts of mineral oil is prepared at room temperature. A mixture of 303 parts (1 equivalent) of the O,O-di(alkyl)phosphorodithioic acid described in Example 2 and 36 parts (0.25 equivalents) of 2-ethylhexanoic acid is added over 10 minutes and a slight exotherm is observed. When addition is complete, the temperature is increased to 80°C for 3 hours. The mixture is vacuum stripped at 100°C and filtered.

Example C-5

Following the procedure of Example C-4, a product is prepared from 383 parts (1.2 equivalents) of a dialkyl phosphorodithioic acid containing 65% isobutyl and 35 % amyl groups, 43 parts (0.3 equivalent) of 2-ethylhexanoic acid, 71 parts (1.73 equivalents) of zinc oxide and 47 parts of mineral oil. The resulting metal salt, obtained as a 90% solution in mineral oil, contains 11.07% zinc.

Example C-6

Following the procedure of Example C-4, a product is prepared from 474 parts (1.2 equivalents) of a dialkylphosphorodithioic acid containing 80% 2-ethylhexyl groups and 20% isobutyl groups, 43 parts (0.3 equivalent) of 2-ethylhexanoic acid, 80 parts (1.95 equivalents) of zinc oxide and 57 parts of mineral oil. The resulting metal salt is obtained as a 91% solution in mineral oil.

Example C-7

A mixture of 118 parts (2.8 equivalents) of zinc oxide, 25 parts (0.25 equivalent) of sebacic acid and 72 parts of mineral oil is stirred at room temperature and a mixture of 584 parts (2 equivalents) of the dialkylphosphorodithioic acid of Example 2 and 36 parts (0.25 equivalent) of 2-ethyl-hexanoic acid is added over 30 minutes. The temperature increases to 65°C during the addition. The solution is heated to 80°C for 3 hours and vacuum stripped at 180°C. The residue is filtered to yield the desired metal salt (90% solution in mineral oil) containing 11.7% zinc.

Example C-8

A product is prepared by the procedure of Example C-4 except that an equivalent amount of oleic acid is substituted for the 2-ethylhexanoic acid.

Examples C-9 to C-11

Triphenyl phosphite is heated with a zinc salt of a mixture of a dialkylphosphorodithioic acid and a carboxylic acid. The dialkylphosphorodithioic acid used in the preparation of the zinc salt is itself prepared by the reaction of at least one alcohol with phosphorus pentasulfide which contains a stoichiometric excess of sulfur. The reaction conditions and results are given in Table I. The salts are prepared by reacting zinc oxide with 4 equivalents of the dialkylphosphorodithioic acid and 1 equivalent of the carboxylic acid, a total of 1.3 equivalents of zinc oxide being used per equivalent of acid. The reactions are carried out in a small amount of mineral oil as diluent.

TABLE I

Example	$R^1O(R^2O)P(S)SH$ R^1, R^2	R^3COOH R^3	% S in P_2S_5	Parts $(C_6H_5O)_3P$ per 100 parts salt	Temp., °C	Time, Hours
C-9	2-Ethylhexyl	3-Heptyl	72.6	3.4	120	3
C-10	2-Ethylhexyl	3-Heptyl	72.3-72.7	6.5	130	3 1/2
C-11	2-Ethylhexyl	3-Heptyl	72.3-72.7	7.5	130	4

Example C-12

A reaction mixture is prepared by the addition of 3120 parts (24.0 moles) of 2-ethylhexanol and 444 parts (6.0 moles) of isobutyl alcohol. With nitrogen blowing at 1.0 cubic feet per hour, 1540 parts (6.9 moles) of P_2S_5 is added to the mixture over a two-hour period while maintaining the temperature at 60-78°C. The mixture is held at 75°C for one hour and is stirred an additional two hours while cooling. The mixture is filtered through diatomaceous earth. At 25°C, 4745 parts (12.5 moles) of this filtered mixture is added to a mixture of 590 parts (14.4 moles) of ZnO, 114 parts of a commercially available mixture of C_{15-18} alpha-olefins and 457 parts of diluent oil over a thirty minute period. The exotherm increases the temperature to 70°C. The mixture is heated to 85°C and maintained at that temperature for three hours. The mixture is stripped to 110°C at 25 mm. Hg. The mixture is filtered twice through diatomaceous earth.

Example C-13

A slurry is prepared by the addition of 486.6 parts (11.86 equivalents) of ZnO and 243.1 parts diluent oil. With medium speed stirring 1204 parts (3.6 equivalents) of O,O-di(4-methyl-2-pentyl)phosphorodithioic acid are added to the slurry and the temperature of the resulting mixture is increased from 56°C to 87°C over a period of 20 minutes. 2407 parts (7.2 equivalents) of O,O-di-(4-methyl-2-pentyl)phosphorodithioic acid are added to the mixture. The temperature of the mixture is maintained at 86°C for 4 hours. 500 parts of the mixture are poured off. The remaining 3831 parts of mixture are mixed with 156.04 parts of a commercially available mixture of C_{15-18} alpha-olefins. The mixture is stripped to 105°C at 15 mm. Hg. The temperature of the mixture is increased from 22°C to 105°C over a 3 1/2 hour period. The mixture is held at 105°C under a nitrogen flow of 0.5 cubic feet per hour for an additional two hours before

being allowed to cool. The mixture is cooled and filtered through diatomaceous earth. The filtrate is the product.

Example C-14

The process of Example C-1 is repeated replacing the zinc oxide with about 1.15 equivalents of cuprous oxide.

Example C-15

The process of Example C-1 is repeated employing O,O-di(2-ethylhexyl)phosphorodithioic acid.

Example C-16

The process of Example C-15 is repeated employing 1 equivalent of copper (I) oxide for each equivalent of zinc oxide.

Examples C-17-20

The process of Example C-15 is repeated employing 1 equivalent of:

Example No.	Metal Compound
17	Manganese (IV) oxide
18	Nickel (II) oxide
19	Molybdenum (VI) oxide
20	Tin (II) oxide

Additional representative examples of metal salts useful as component (C) in the compositions of this invention appear in the patents and publications herein incorporated by reference. Other examples will occur to one skilled in the art.

(D) The Triazole

The triazole which may be used in this invention may be benzotriazole and alkyl-substituted benzotriazole. The alkyl substituent generally contains up to 15 carbon atoms, preferably up to 8 carbon atoms. In addition to the alkyl substituent, the triazoles may contain other

substituents on the aromatic ring such as halogens and nitro groups. Examples of suitable compounds are benzotiazole and the tolyltriazoles, ethylbenzotriazoles, hexylbenzotriazoles, octylbenzotriazoles, chlorobenzotriazoles and nitrobenzotriazoles. Benzotriazole and tolyltriazole are particularly preferred.

The amount of triazole included in the composition generally is less than 5%, more often less than 1% by weight. When the composition of the invention is to be used in a lubricating oil such as a hydraulic fluid, only small amounts of the triazole compound are required to obtain improved hydrolytic stability. Generally the composition of the invention will contain an amount of triazole compound which will provide an additive concentrate for lubricants and functional fluid which contains as little as 100 ppm of the triazole and preferably less than 50 ppm of the triazole. When formulated into finished lubricants and functional fluids, the compositions of the invention are prepared to provide the lubricant or functional fluid with a stabilizing amount of the triazole which generally is less than 20 ppm, and may be less than 3 ppm of finished lubricant or functional fluid.

It is sometimes useful to incorporate, on an optional, as-needed basis other known additives which include, but are not limited to, dispersants, detergents, antioxidants, anti-wear agents, extreme pressure agents, emulsifiers, demulsifiers, foam inhibitors, friction modifiers, anti-rust agents, corrosion inhibitors, viscosity improvers, pour point depressants, dyes, and solvents to improve handleability which may include alkyl and/or aryl hydrocarbons. These optional additives may be present in various amounts depending on the intended application for the final product or may be excluded therefrom.

Dispersants include, but are not limited to, hydrocarbon substituted succinimides, succinamides, carboxylic esters, Mannich dispersants and mixtures thereof as well as materials functioning both as dispersants and viscosity improvers. The dispersants include nitrogen-containing carboxylic dispersants, ester dispersants, Mannich dispersants or mixtures thereof. Nitrogen-containing carboxylic dispersants are prepared by reacting a hydrocarbyl carboxylic acylating agent (usually a hydrocarbyl substituted succinic anhydride) with an amine (usually a polyamine). Ester dispersants are prepared by reacting a polyhydroxy compound with a hydrocarbyl carboxylic acylating agent. The ester dispersant may be further treated with an amine. Mannich dispersants are prepared by reacting a hydroxy aromatic compound with an amine and aldehyde. The dispersants listed above may be post-treated with reagents such as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon substituted succinic anhydride, nitriles, epoxides, boron compounds, phosphorus compounds and the like. These dispersants are generally referred to as ashless dispersants even though they may contain elements such as boron or phosphorus which, on decomposition, will leave a non-metallic residue.

Extreme pressure agents and corrosion- and oxidation-inhibiting agents include chlorinated compounds, sulfurized compounds, phosphorus containing compounds including, but not limited to, phosphosulfurized hydrocarbons and phosphorus esters, metal containing compounds and boron containing compounds.

Chlorinated compounds are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax.

Examples of sulfurized compounds are organic sulfides and polysulfides such as benzyl disulfide, bis(chlorobenzyl)disulfide, dibutyl tetrasulfide,

sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, and sulfurized terpene.

Phosphosulfurized hydrocarbons include the reaction product of a phosphorus sulfide with turpentine or methyl oleate.

Phosphorus esters include dihydrocarbon and trihydrocarbon phosphites, phosphates and metal and amine salts thereof.

Phosphites may be represented by the following formulae:

$$R_5O - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}} - OR_5$$

or

$$(R_5O)_3P$$

wherein each R_5 is independently hydrogen or a hydrocarbon based group, provided at least one R_5 is a hydrocarbon based group.

Preferably each R_5 is independently a hydrogen or hydrocarbon based group having from 1 to about 24, more preferably from 1 to about 18, and more preferably from about 2 to about 8 carbon atoms, provided that at least one R_5 is a hydrocarbon based group, Each R_5 may be independently alkyl, alkenyl or aryl. When R_5 is aryl it contains at least 6 carbon atoms; preferably 6 to about 18 carbon atoms. Examples of alkyl or alkenyl groups are propyl, butyl, hexyl, heptyl, octyl, oleyl, linoleyl, stearyl, etc. Examples of aryl groups are phenyl, naphthyl, heptylphenyl, etc. Preferably each R_5 is independently propyl, butyl, pentyl, hexyl, heptyl, oleyl or phenyl, more preferably butyl, oleyl or phenyl and more preferably butyl or oleyl.

The R_5 groups may also comprise a mixture of hydrocarbyl groups derived from commercial alcohols. Examples of preferred monohydric alcohols and alcohol mixtures include commercially available "Alfol" alcohols marketed by Continental Oil Corporation. Alfol 810 is a mixture containing alcohols consisting essentially of straight-chain, primary alcohols having 8 to 10 carbon atoms. Alfol 812 is a mixture comprising mostly C_{12} fatty alcohols. Alfol 1218 is a mixture of synthetic, primary, straight-chain alcohols having from 12 to 18 carbon atoms. Alfol 20+ alcohols are mixtures of 18-28 primary alcohols having mostly, on an alcohol basis, C_{20} alcohols as determined by GLC (gas-liquid-chromatography).

Another group of commercially available alcohol mixtures includes the "Neodol" products available from Shell Chemical Company. For example, Neodol 23 is a mixture of C_{12} and C_{13} alcohols; Neodol 25 is a mixture of C_{12} and C_{15} alcohols; and Neodol 45 is a mixture of C_{14} and C_{15} linear alcohols. Neodol 91 is a mixture of C_9, C_{10} and C_{11} alcohols.

Phosphites and their preparation are known and many phosphites are available commercially. Particularly useful phosphites are dibutylhydrogen phosphite, trioleyl phosphite and triphenyl phosphite. Preferred phosphite esters are generally dialkyl hydrogen phosphites.

A number of dialkyl hydrogen phosphites are commercially available, such as lower dialkyl hydrogen phosphites, which are preferred. Lower dialkyl hydrogen phosphites include dimethyl, diethyl, dipropyl, dibutyl, dipenyl and dihexyl hydrogen phosphites.

Phosphate esters include mono-, di- and trihydrocarbon-based phosphates of the general formula

$$(R_5O)_3PO$$

wherein R_5 is as defined for the phosphites described hereinabove. Examples include mono-, di- and trialkyl ; mono-, di and triaryl and mixed alkyl and aryl. Specific, non-limiting examples include, tri lower alkyl phosphate, dialkyl phosphates, and the like. Particularly preferred are the reaction products of phosphorus pentoxide (P_2O_5) with alcohols in a ratio of 3 hydroxyl groups to one P_2O_5 yielding a mixture of mono- and dialkyl phosphates. Also available or readily prepared by known techniques are diheptyl, dicyclohexyl, pentylphenyl, dipentylphenyl, tridecyl, distearyl, dimethyl naphthyl, oleyl 4-pentylphenyl, polypropylene (molecular weight 500)-substituted phenyl, and diisobutyl-substituted phenyl phosphites. Also mixed alkyl hydrogen phosphites are useful in the present invention. Examples of mixed alkyl hydrogen phosphites include ethyl, butyl; propyl, pentyl; and methyl, pentyl hydrogen phosphites.

Metal containing compounds include metal thiocarbamates, such as zinc dioctyldithiocarbamate, and barium heptylphenyl dithiocarbamate and molybdenum compounds.

Boron containing compounds include borate esters and boron-nitrogen containing compounds prepared, for example, by the reaction of boric acid with a primary or secondary alkyl amine.

Viscosity improvers include, but are not limited to, polyisobutenes, polymethacrylate acid esters, polyacrylate acid esters, diene polymers, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers, polyolefins and multifunctional viscosity improvers.

Pour point depressants are a particularly useful type of additive often included in the lubricating oils described herein. See for example, page 8 of "Lubricant Additives" by C. V. Smalheer and R. Kennedy Smith (Lesius-Hiles Company Publishers, Cleveland, Ohio, 1967).

Anti-foam agents used to reduce or prevent the formation of stable foam include silicones or organic polymers. Examples of these and additional anti-foam compositions are described in "Foam Control Agents", by Henry T. Kerner (Noyes Data Corporation, 1976), pages 125-162.

These and other additives are described in greater detail in U.S. Patent 4,582,618 (column 14, line 52 through column 17, line 16, inclusive), herein incorporated by reference for its disclosure of other additives that may be used in combination with the present invention.

The components may be blended together in any suitable manner and then admixed, for example with a diluent to form a concentrate as discussed below, or with a lubricating oil, as discussed below. Alternatively, components can be admixed separately with such diluent or lubricating oil. In preparing concentrates, it is preferred that the triazole, if used, be dissolved first in the diluent by heating to a temperature of about 80-90°C followed by cooling before the remaining components are blended into the diluent. The blending technique for mixing the components is not critical and can be effected using any standard technique, depending upon the specific nature of the materials employed. In general, blending can be accomplished at room temperature; however, blending can be facilitated by heating the components.

As previously indicated, the compositions of the present invention are useful as additives for lubricants and functional fluids. They can be employed in a variety of lubricants based on diverse oils of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. The lubricants include crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, including automobile and truck engines, two-cycle

engines, aviation piston engines, marine and railroad diesel engines, and the like. Also contemplated are lubricants for gas engines, stationary power engines and turbines and the like. Transaxle lubricants, gear lubricants, metal-working lubricants and other lubricating oil and grease compositions, as well as functional fluids such as hydraulic fluids and automatic transmissions fluids, benefit from the incorporation therein of the compositions of the present invention. As discussed hereinabove, this invention provides special benefits when the composition is exposed to water.

The lubricating compositions and methods of this invention employ an oil of lubricating viscosity, including natural or synthetic lubricating oils and mixtures thereof. Natural oils include animal oils, vegetable oils, mineral lubricating oils, solvent or acid treated mineral oils, and oils derived from coal or shale. Synthetic lubricating oils include hydrocarbon oils, halo-substituted hydrocarbon oils, alkylene oxide polymers, esters of carboxylic acids and polyols, esters of polycarboxylic acids and alcohols, esters of phosphorus-containing acids, polymeric tetrahydrofurans, silicon-based oils and mixtures thereof.

Specific examples of the oils of lubricating viscosity are described in U.S. Patent 4,326,972 and European Patent Publication 107,282, both herein incorporated by reference for their disclosures relating to lubricating oils. A basic, brief description of lubricant base oils appears in an article by D. V. Brock, "Lubricant Base Oils", Lubrication Engineering, volume 43, pages 184-185, March, 1987. This article is herein incorporated by reference for its disclosures relating to lubricating oils. A description of oils of lubricating viscosity occurs in U.S. Patent 4,582,618 (column 2, line 37 through column 3, line 63, inclusive), herein incorporated by reference for its disclosure to oils of lubricating viscosity.

Component (A) and component (B) are generally used in relative amounts of A:B ranging from about 5:1 to about 1:5, more often from about 2:1 to about 1:2, by weight.

When component (C) is present, it is generally used in amounts relative to component (A) ranging from about A:C = 1:40 to 2:1, preferably from about 1:20 to about 1:1, more preferably from about 1:10 to about 1:1.

Component (A) is used in the lubricating oil compositions of this invention in amounts ranging from about 0.01 to about 5% by weight, often up to about 2% by weight. A preferred range is from about 0.01 to about 1% by weight of the total weight of the composition.

Components (B) and (C) are utilized in amounts within the above-specified amounts relative to component (A).

The following examples illustrate compositions of the present invention. The amount of each component in the Examples also reflects the amount of oil present in the indicated components.

TABLE II

Additive Concentrates

Component	Example No. (Weight %) 1	2	3	4	5
Product of Example C-11	62.17			62.17	
Product of Example C-2			64.3		
Product of Example C-13					58.78
Tolyltriazole	0.18			0.18	
Benzotriazole			0.14		
Hexylbenzotriazole					0.24
Sodium Petroleum Sulfonate	4.94		4.65	4.94	3.98
Hindered Phenol	21.18		19.9	21.18	18.96
Benzotriazole Derived Copper Corrosion Inhibitor	0.55		0.52	0.55	0.49
Product of Example A-15			4.75		
Product of Example A-11	6.18			4.12	
Product of Example A-2		72.2			
Product of Example A-6					6.6
Mineral Oil Diluent	0.39		0.66	0.39	0.95
Polyacrylate Antifoam	2:35		2.23	2.35	2.37
Product of Example B-7	2.06		2.84	4.12	
Product of Example B-2		27.8			
Product of Example B-4					7.56

As indicated hereinabove, the compositions of this invention are useful as additives for a wide variety of lubricating compositions. Preferred lubricating compositions are functional fluids, with hydraulic fluids being particularly preferred. The following are non-limiting examples of lubricating compositions of this invention.

Example 6

To a 100 neutral mineral oil basestock is added, with mixing and gentle heating, 1% by weight of the product of Example A-1, 0.3% by weight of the product of Example B-4, and 0.01 percent by weight of a silicone antifoam.

Example 7

To a mineral oil basestock (250 neutral) is added 0.85 percent by weight of the additive concentrate of Example 1.

Example 8

Example 7 is repeated except additive concentrate of Example 1 is replaced with that of Example 4.

Example 9

To the lubricating oil composition of Example 6 is added 0.05% by weight of the product of Example C-1.

Example 10

To Sun Tulsa ISO 46 base oil is added 0.81 percent by weight of the additive concentrate of Example 3.

Example 11

To Sun Tulsa ISO 46 base oil is added 0.1 percent by weight of the additive concentrate of Example 2.

Example 12

Example 7 is repeated except the additive concentrate of Example 4 replaces that of Example 1.

Example 13

To a hydraulic fluid basestock (ISO 46) is added 0.1 parts of dibutyl hydrogen phosphite, 0.01 parts of tolyltriazole, 0.1 parts of a magnesium salicylate, 0.05 parts of the reaction product of propylene oxide with tetrapropenyl succinic anhydride, 0.2 parts of tricresyl phosphate, 0.25 parts of hindered phenol, 0.25 parts of di(nonylphenyl) amine and 0.05 parts of the product of Example B-7.

Example 14

A hydraulic fluid is prepared according to the procedure of Example 13 replacing 0.05 parts of the product of Example B-7 with 0.03 parts of the product of Example B-6.

Example 15

A composition comprising an oil of lubricating viscosity, 0.85 percent by weight of the product of Example A-4, 0.15 parts of the product of Example B-6, 0.2 parts of hindered phenol, 0.002 percent by weight of tolyltriazole and 0.01 percent by weight of an organic polymer antifoam.

Example 16

The composition of Example 7 replacing the product of Example C-11 with that of Example C-16.

The filterability of hydraulic fluids can be determined employing the AFNOR E48-690/1 test published by l'Association Francaise DeNormalisation, Tour Europe Cedex 7 92 080 Paris-La Defense, France. This test

consists of filtering, under constant pressure, at constant temperature, through a membrane with a determined absolute stopping power, a specified volume of fluid contained in a container of defined dimensions. This test employs an essentially uncontaminated fluid.

Filterability indices of the fluid (IF_1, and IF_2) are defined for a given fluid by the ratios:

$$IF_1 = \frac{T_{300} - T_{200}}{2\ T_{50}} \quad \text{and } IF_2 = \frac{T_{300} - T_{200}}{2\ (T_{100} - T_{50})}$$

in which

T_{300} is the passage time, through the membrane, of 300 cm^3 of fluid,

T_{200} is the passage time, through the membrane, of 200 cm^3 of fluid,

T_{100} is the passage time, through the membrane, of 100 cm^3 of fluid,

T_{50} is the passage time, through the membrane, of 50 cm^3 of fluid.

This ratio therefore consists of comparing the filtration speeds of the fluid in the course of the test. These ratios as well as the filtration speeds of the various segments for each sample are indicative of the ease of filtration of the fluids.

A modification of this test entails the use of a water-treated fluid. To the fluid is added a fixed amount of water, the mixture is agitated, then stored. After the aging period, the water-treated fluid is evaluated as above.

The results of the filtration of the water-free and the water-containing fluids are compared. It has been observed that when the fluids are contaminated with water, filtration of fluids of the present invention is significantly improved compared to similar fluids that do not contain the acidic material, component (B).

It has also been observed that when a fluid contains zinc, usually as a zinc salt, depletion of zinc may occur when the fluid is exposed to ASTM D-943 test conditions, which are oxidation conditions including the presence of water. The compositions of this invention resist depletion of zinc under those test conditions.

While this invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the disclosure. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

What is claimed is:

1. A composition comprising a major amount of an oil of lubricating viscosity and minor amounts of

(A) a metal salt selected from the group consisting of sulfonates, phenates, carboxylates and mixtures thereof; and

(B) an aliphatic carboxylic acid or an anhydride thereof, wherein the aliphatic group contains at least about 20 carbon atoms,

wherein (B) is present in an effective amount to improve wet filterability of the composition.

2. The composition of claim 1 wherein component (A) is an overbased metal salt.

3. The composition of claim 1 wherein component (B) is a polyolefin substituted succinic acid or anhydride, ester acid or lactone acid.

4. The composition of claim 3 wherein the polyolefin substituent is a polyethylene group, a polypropylene group, a polybutylene group or mixtures thereof.

5. The composition of claim 1 wherein the metal is an alkali metal, an alkaline earth metal, copper or zinc.

6. The composition of claim 2 wherein the metal salt is a sulfonate, carboxylate or mixtures thereof.

7. The composition of claim 2 wherein the metal salt is a phenate.

8. The composition of claim 6 wherein component (A) is a carboxylate.

9. The composition of claim 5 wherein the metal is an alkali or alkaline earth metal.

10. The composition of claim 9 wherein the metal is sodium, potassium, calcium or magnesium.

11. The composition of claim 7 wherein the metal is an alkali or alkaline earth metal and the phenate is a sulfurized phenate.

12. The composition of claim 1 which further comprises (C) a metal salt of (C)(I) at least one organic phosphorus acid or a mixture of (C)(I) at least one organic phosphorus acid and (C)(II) at least one carboxylic acid.

13. The composition of claim 1 further comprising a phosphite.

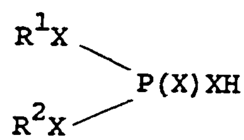
14. The composition of claim 13 wherein the phosphite is selected from the group consisting of dialkyl hydrogen phosphites, trialkyl phosphites and triaryl phosphites.

15. The composition of claim 8 wherein the metal is an alkali metal, an alkaline earth metal, copper or zinc.

16. The composition of claim 15 wherein the metal salt is an overbased metal salicylate.

17. The composition of claim 13 wherein the metal salt is an overbased alkaline earth metal salicylate.

18. The composition of claim 12 wherein (C)(I) the phosphorus acid is at least one acid of the general formula:



(I)

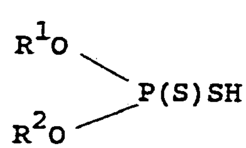
wherein R^1 and R^2 are the same or different and each of R^1 and R^2 is H or a hydrocarbon-based group with the proviso that at least one of R^1 and R^2 is a hydrocarbon-based group, and each X is independently S or O; and (C)(II) the carboxylic acid is an aliphatic or alicyclic carboxylic acid containing from 2 to about 40 carbon atoms.

19. The composition of claim 18 wherein each of R^1 and R^2 is independently an alkyl group containing from about 3 to about 50 carbon atoms.

20. The composition of claim 11 wherein component (A) is a calcium phenate.

21. The composition of claim 18 wherein both R^1 and R^2 are hydrocarbon-based groups.

22. The composition of claim 18 wherein the phosphorus acid (C)(I) has the general formula



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23. A composition comprising

(A) an alkali or an alkaline earth metal phenate;

(B) an aliphatic substituted succinic acid or an anhydride thereof, wherein the aliphatic group contains from about 30 to about 400 carbon atoms; and

(C) a metal salt of (C)(I) at least one organic phosphorus acid or a mixture of (C)(I) at least one phosphorus acid and (C)(II) at least one carboxylic acid.

24. The composition of claim 23 wherein component (B) is a polyolefin substituted succinic acid or anhydride.

25. The composition of claim 24 wherein the polyolefin substituent is a polyethylene group, a polypropylene group or a polybutylene group or mixtures thereof.

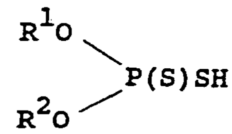
26. The composition of claim 23 wherein component (A) is a sulfurized phenate.

27. The composition of claim 26 wherein component (A) is a calcium phenate.

28. The composition of claim 26 wherein component (A) has a phenol group to sulfur mole ratio ranging from about 2:1 to about 1:2.

29. The composition of claim 25 wherein component (A) contains from about 250% to about 450% of the metal present in the corresponding normal metal phenate.

30. The composition of claim 23 wherein (C)(I) the phosphorus acid is at least one acid of the general formula:



wherein each of R^1 and R^2 is the same or different and each of R^1 and R^2 is independently an alkyl group containing from about 3 to about 50 carbon atoms, and the carboxylic acid is

(C)(II). at least one acid of the general formula:

$$R^3COOH, \qquad (II)$$

wherein R^3 is an aliphatic or alicyclic hydrocarbon-based group.

31. The composition of claim 30 wherein component (C)(II) contains from about 2 to about 40 carbon atoms.

32. The composition of claim 30 wherein R^3 is a saturated aliphatic group.

33. The composition of claim 32 wherein R^3 is a branched alkyl group.

34. The composition of claim 30 wherein each of R^1 and R^2 is 2-ethylhexyl and R^3 is 3-heptyl.

35. The composition of claim 30 wherein the ratio of equivalents of (C)(I) to (C)(II) is between about 0.5:1 and 500:1.

36. The composition of claim 1 wherein the relative amounts of (A):(B) range from about 5:1 to about 1:5 by weight.

37. The composition of claim 12 wherein the weight ratio of (A):(C) is in the range of about 1:40 to about 2:1.

38. The composition of claim 1 which further comprises

(D) a stabilizing amount of at least one triazole selected from the group consisting of benzotriazole and alkyl substituted benzotriazoles containing up to 15 carbon atoms in the alkyl group.

39. The composition of claim 23 wherein component (A) includes at least one hydrocarbon-based group attached to an aromatic moiety, said hydrocarbon-based group having from about 6 to about 80 carbon atoms.

40. The composition of claim 23 wherein the metal of component (C) is a least one of Group I metals, Group II metals, aluminum, tin, cobalt, molybdenum, lead, manganese and nickel.

41. The composition of claim 40 herein the metal of component (C) is zinc.

42. The composition of claim 21 wherein the metal salt (C) is contacted under reaction conditions with at least one phosphite of the general formula

$$(R^4O)_3P$$

wherein each R^4 is independently hydrogen or a hydrocarbon-based group.

43. The composition of claim 23 also containing a basic alkali or alkaline earth metal salt of an organic sulfonic acid.

44. The composition of claim 1 also containing a phenolic antioxidant compound.

45. The composition of claim 1 also containing at least one ashless dispersant.

46. The composition of claim 1 also containing at least one demulsifier.

47. The composition of claim 36 wherein component (A) is present in amounts ranging from about 0.01% to about 1% by weight.

48. A method for improving the wet filterability characteristics of a functional fluid comprising

(A) a major amount of an oil of lubricating viscosity; and

(B) a Group I or Group II metal salt selected from the group consisting of sulfonates, phenates, carboxylates and mixtures thereof,

which method comprises incorporating into said functional fluid a wet filterability improving amount of

(C) an aliphatic carboxylic acid or anhydride thereof wherein the aliphatic group contains at least about 20 carbon atoms.

AMENDED CLAIMS

[received by the International Bureau on 9 November 1992 (09.11.92); original claims 1-48 replaced by amended claims 1-22 (5 pages)]

1. A composition comprising a major amount of an oil of lubricating viscosity and minor amounts of

(A) a metal salt selected from the group consisting of sulfonates, phenates, carboxylates and mixtures thereof; and

(B) an aliphatic carboxylic acid or an anhydride thereof, wherein the aliphatic group contains at least about 20 carbon atoms,

wherein (B) is present in an effective amount to improve wet filterability of the composition.

2. A composition comprising

(A) an alkali or an alkaline earth metal phenate;

(B) an aliphatic substituted succinic acid or an anhydride thereof, wherein the aliphatic group contains from about 30 to about 400 carbon atoms; and

(C) a metal salt of (C)(I) at least one organic phosphorus acid or a mixture of (C)(I) at least one phosphorus acid and (C)(II) at least one carboxylic acid.

3. The composition of any one of claims 1 and 2 wherein component (A) is an overbased metal salt.

4. The composition of any one of the foregoing claims wherein the metal is an alkali metal, an alkaline earth metal, copper or zinc.

5. The composition of claim 1 wherein component (A) is a calcium phenate.

6. The composition of claim 4 wherein component (A) is a sulfurized calcium phenate.

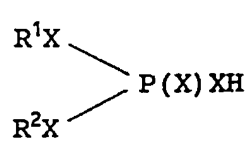
7. The composition of claim 1 wherein component (B) is a polyolefin substituted succinic acid or anhydride, ester acid or lactone acid.

8. The composition of claim 7 wherein the polyolefin substituent is a polyethylene group, a polypropylene group, a polybutylene group or mixtures thereof.

9. The composition of claim 3 wherein the metal salt is an overbased metal salicylate.

10. The composition of any one of the foregoing claims further comprising a phosphite selected from the group consisting of dialkyl hydrogen phosphites, trialkyl phosphites and triaryl phosphites.

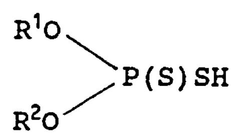
11. The composition of any one of claims 2-10 wherein (C)(I) the phosphorus acid is at least one acid of the general formula:



(I)

wherein R^1 and R^2 are the same or different and each of R^1 and R^2 is H or a hydrocarbon-based group with the proviso that at least one of R^1 and R^2 is a hydrocarbon- based group, and each X is independently S or O; and (C)(II) the carboxylic acid is an aliphatic or alicyclic carboxylic acid containing from 2 to about 40 carbon atoms.

12. The composition of claim 11 wherein (C)(I) the phosphorus acid is at least one acid of the general formula:



wherein each of R^1 and R^2 is the same or different and each of R^1 and R^2 is independently an alkyl group containing from about 3 to about 50 carbon atoms, and the carboxylic acid is

(C)(II) at least one acid of the general formula:

$$R^3COOH, \qquad (II)$$

wherein R^3 is an aliphatic or alicyclic hydrocarbon-based group containing from about 2 to about 40 carbon atoms.

13. The composition of any one of claims 2-12 wherein the ratio of equivalents of (C)(I) to (C)(II) is between about 0.5:1 and 500:1.

14. The composition of any one of the foregoing claims wherein the relative amounts of (A):(B) range from about 5:1 to about 1:5 by weight.

15. The composition of any one of claims 2-14 wherein the weight ratio of (A):(C) is in the range of about 1:40 to about 2:1.

16. The composition of claim 15 wherein the metal of component (C) is a least one of Group I metals, Group II metals, aluminum, tin, cobalt, molybdenum, lead, manganese and nickel.

17. The composition of claim 16 wherein the metal of component (C) is zinc.

18. The composition of claim 15 wherein the metal salt (C) is contacted under reaction conditions with at least one phosphite of the general formula

$$(R^4O)_3P$$

wherein each R^4 is independently hydrogen or a hydrocarbon-based group.

19. The composition of claim 2 also containing at least one basic alkali or alkaline earth metal salt of an organic sulfonic acid.

20. The composition of any one of the foregoing claims also containing at least one member selected from the group consisting of a phenolic antioxidant compound, an ashless dispersant and a demulsifier.

21. The composition of claim 14 wherein component (A) is present in amounts ranging from about 0.01% to about 1% by weight.

22. A method for improving the wet filterability characteristics of a functional fluid comprising

(A) a major amount of an oil of lubricating viscosity; and

(B) a Group I or Group II metal salt selected from the group consisting of sulfonates, phenates, carboxylates and mixtures thereof,

which method comprises incorporating into said functional fluid a wet filterability improving amount of

(C) an aliphatic carboxylic acid or anhydride thereof wherein the aliphatic group contains at least about 20 carbon atoms.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/05928

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C10M141/10; C10M163/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C10M

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

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III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category°	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	EP,A,0 096 539 (EXXON RESEARCH AND ENGINEERING CO.) 21 December 1983	1-12, 15-17, 20,36, 37,44-48
	see page 12, line 22 - page 13, line 5; claims 1-8	
Y		12-14, 18,19, 21-35, 38-43

X	FR,A,2 512 831 (THE LUBRIZOL CORP.) 18 March 1983	1-6, 8-10, 12-17, 36,37, 44-48
	see page 13, line 1 - page 18; claims 1-15	

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° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
01 JANUARY 1980	21.09.92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	ROTSAERT L.D.C.

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International Application No PCT/US 92/05928

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	US,A,4 466 894 (K.B.GROVER) 21 August 1984 cited in the application see column 17, line 9 - line 38; claims 1-33	12-14, 18,19, 21-35, 38-43
P,X	EP,A,0 462 319 (THE LUBRIZOL CORP.) 27 December 1991 see page 33, line 50 - page 34, line 33 see page 37, line 30 - line 38; claims 1-18	1-48
A	US,A,3 261 782 (D.J.ANDERSON) 19 July 1966 see claim 1	3

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9205928
SA 62412

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 01/09/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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		CA-A-	1197833	10-12-85
		DE-A-	3375156	11-02-88
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		GB-A-	1037985	

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82